DESIGN AND IMPLEMENTATION OF TUNABLE DIODE LASER-BASED
MULTI-SPECIES AND ENTHALPY SENSING IN EXTREME ENVIRONMENTS

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Abstract

Scanned-direct absorption spectroscopy (DAS) and scanned-wavelength modulation spectroscopy (WMS) were implemented for sensing in two distinct and extreme environments. A comparison of scanned-DAS and scanned-WMS was completed within the context of a biomass gasification pilot scale facility, while scanned-DAS was implemented and optimized to increase sensing capabilities in the mixing volume (MV) of the 60 MW Interaction Heating Facility (IHF) at NASA Ames Research Center (ARC).

In the biomass gasification study, a demonstration of in situ laser-absorption-based sensing of H$_2$O, CH$_4$, CO$_2$, and CO mole fraction is reported for the product gas line of a biomass gasifier. Spectral simulations were used to select candidate sensor wavelengths that optimize sensitive monitoring of the target species while minimizing interference from other species in the gas stream. A prototype sensor was constructed and measurements were performed in the laboratory at Stanford to validate sensor performance. Field measurements then were demonstrated in a pilot scale biomass gasifier at WestBiofuels in Woodland, California. The performance of a prototype sensor was compared for the two sensing strategies, scanned-DAS and scanned-WMS. The lasers used had markedly different wavelength tuning response to injection current, and modern distributed feedback lasers (DFB) with nearly linear tuning response to injection current were shown to be superior, leading to guidelines for laser selection for sensor fabrication. The potential for non-absorption loss in the transmitted laser intensity from particulate scattering and window fouling encouraged the use of normalized WMS measurement schemes. The complications of using normalized WMS for relatively large values of absorbance and its
mitigation are discussed. A method for reducing adverse sensor performance effects of a time-varying WMS background signal is also presented. The laser absorption sensor provided measurements with the sub-second time resolution needed for gasifier control and more importantly provided precise measurements of H₂O in the gasification products, which can be problematic for the typical gas chromatography sensors used by industry.

The IHF at NASA ARC is a critical facility used to study and characterize thermal protection systems (TPS) of reentry spacecraft. The IHF generates an electrical arc to energize room temperature air, which is then forced through a converging-diverging nozzle. Material and model test pieces are then subjected to the stagnation environment of the flow stream. The efforts at ARC focused on characterizing the mixing of add-air in the MV of the IHF. The implementation of scanned-DAS in the MV of the IHF first involved characterizing the existing sensor and developing an optimized second-generation sensor. Conditions in the IHF, in the mixing volume (MV) where this study focused its optical measurements, range from 5,000 to 7,000 K and 1 to 9 atm. Path-average line-of-sight measurements of temperature and enthalpy were inferred using an electronic atomic oxygen transition near 777 nm. The scanned-DAS sensor was optimized to capture high add-air and high-pressure conditions that previously had not been measurable. Characterization of the external cavity diode laser yielded an expanded laser tuning range of 3 cm⁻¹. The increased tuning range allowed for full absorbance profile resolution at the maximum pressure test condition in the IHF MV. Increased scan frequency of the laser allowed for suppression of mechanical vibration-induced noise and increased temporal resolution of the sensor. Enhanced sensor capabilities confirmed uniform flow and flat temperature immediately upstream of the arcjet’s converging-diverging nozzle inlet. Less
uniform and parabolic temperature profiles were observed immediately downstream of add-air injection. This arcjet facility implements injection of room temperature air, i.e. add-air, to tune the bulk and centerline enthalpy generated at the nozzle exit. The add-air is injected upstream of a mixing volume that allows for mixing upstream of the nozzle inlet. Optical access is integrated into the MV at four axial locations along its length. Centerline temperatures at an axial location downstream of add-air injection confirmed the need for mixing beyond the MV entrance. This validated the need for installation of the MV to achieve uniform flow. Enthalpy measurements ranged from 16 to 27 MJ/kg and are in agreement with the IHF’s current enthalpy measurement methods. This confirmed the observed reduction in achievable enthalpy after installation of the mixing volume. Centerline measurements quantified the mixing process for various add-air conditions indicating an opportunity for enthalpy recapture. Axial locations of sufficient mixing were identified and provide a potential for reduction of the MV length and thus improved facility performance. Optimization of this sensor will enable future use by non-experts to provide critical data on the arcjet environment in the IHF, thereby enhancing arcjet test results and leading to greater reliability of spacecraft TPS designs.
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# Table of Contents

Abstract ................................................................................................................................. iv

Acknowledgements ............................................................................................................... vii

Table of Contents ............................................................................................................... ix

List of Tables ....................................................................................................................... xi

List of Figures ...................................................................................................................... xii

1. Introduction ....................................................................................................................... 1

1.1 Renewable Energy Resources ....................................................................................... 1

1.1.1 Biomass Gasifier ....................................................................................................... 5

1.2 Advanced Thermal Protection Systems ........................................................................... 9

2. Absorption Spectroscopy Theory and Techniques ............................................................. 14

2.1 Absorption Spectroscopy Theory .................................................................................... 14

2.2 Scanned-Direct Absorption Spectroscopy ..................................................................... 18

2.3 Scanned-Direct Wavelength Modulation Absorption Spectroscopy ............................ 20

2.4 Single-Line Thermometry .............................................................................................. 21

3. Multi-Species Sensor Design ........................................................................................... 25

3.1 Design and Implementation ............................................................................................ 25

3.2 Practical Considerations for WMS sensor design ......................................................... 35

4 Atomic Oxygen Sensor Optimization ............................................................................... 39

5. Biomass Gasifier: Multi-Species Sensing ....................................................................... 45
List of Tables

Table 3.1 Mole fraction of major species in producer gas products of biomass gasification.

Table 3.2 Equivalent mole fraction of 2/1/ non-absorbing background signal and a cross-section independent measure of uncertainty. As expected, equivalent mole fraction increases with increased modulation frequency. Although the high equivalent mole fraction values for CO can be subtracted and accounted for, it results in a high sensitivity to changes in scanned-WMS background, which leads to reduced sensor performance.

Table 5.1 Static cell measurements and uncertainty for 0.24 second averaging.

Table 5.2 Static cell measurement uncertainty for WMS for 0.24 second averaging.

Table 5.3 Relative mole fraction percent uncertainties for scanned-DAS (U_{DAS}) and scanned-WMS (U_{WMS}) for 0.24 second averaging from fits to absorption line shapes acquired in field measurements in West Biofuel producer gas. Mole fraction values that correspond to these uncertainties are contained in Figure 5.2.
List of Figures

Figure 1.1 (a) Sketch of the fast circulation fluidized bed biomass gasifier at West Biofuels where red arrows show the biomass input, blue the steam input, cyan the air input, green the producer gas output, and orange the flue gas exhaust. The bed material is illustrated by the black dots. (b) Photo of the pilot-scale gasifier illustrating flow paths with the same arrow color code. Further details on the gasification process can be found in [1], [2].

Figure 1.2 Absorption cell flow path for the West Biofuels gasifier with temperature controlled plumbing to match the producer gas line. The entire producer gas stream is diverted through the cell for laser absorption measurements of H₂O, CH₄, CO₂ and CO.

Figure 1.3 Add-air mixing volume consists of add-air, optical, and spacer disks. A typical optical disk is shown in the downstream view. Line-of-sight B is located at the centerline.

Figure 2.1 The gas flow cell used to make measurements at WestBiofuels was also used as a reference cell. It allowed for spectroscopy measurements that validated fundamental spectroscopic parameters including linestrength. It also validated the multi-species sensor measurements by flowing known flow quantities of the species under investigation.

Figure 2.2 Reference cell used for calibrating atomic oxygen sensor with respect to transition linecenter. This type of cell requires a high-power radio frequency source and is limiting in terms of the quantitative value that it can provide.
**Figure 2.3** Experimentally measured and Voigt fit absorbance profile of an atomic oxygen transition. At the pressure shown, $P = 4.1$ atm, the laser must be scanned at least over a range of at least 2 cm$^{-1}$ in order to accurately calculate the integrated area of the transition that is needed to infer temperature.

**Figure 3.1** Four lasers, one for each target species in the gas mixture, are combined on an optical fiber (wavelength division multiplexer), collimated into a free-space beam and directed through a gas mixture. The transmitted light is collected and focused onto a detector. The laser controller time-multiplexes the four lasers, so that only one laser is operating at a time, and sequential measurements are made at rate of 50 Hz.

**Figure 3.2** Simulations at 300, 350, and 400K for the absorption spectrum of producer gas at 1atm for a 1m path length in the region of the wavelengths selected for the sensor, where H$_2$O, CH$_4$, CO$_2$ and CO can be selectively monitored.

**Figure 3.3** Illustration of the time-multiplexed four laser sensor drive signals. Each laser is scanned for 5 ms on a 20 ms period. Each trace in the lower panel for DAS includes 0.25 ms of the scan below the laser threshold to obtain a thermal background measurement on the detector. The upper panel shows the drive signals for scanned WMS (modulated at 10 kHz).

**Figure 4.1** The laser output is split into four equal-power beams and pitched across the arc column.

**Figure 4.2 a)** Absorbance profile of the reference cell and **b)** laser tuning range as a function of laser scan frequency.
Figure 5.1 Wavelength-scanned DAS measurements (averaged over 0.24 seconds) with Voigt line shape fits taken in the West Biofuels gasifier; the difference between fit and measurement was used to determine measurement uncertainty. Typical mole fraction values for these fits are those contained in Figure 5.2.

Figure 5.2 Wavelength-scanned DAS (left panel) and wavelength-scanned WMS (right panel) measurements during biomass gasification.

Figure 5.3 Wavelength-scanned DAS (left panel) and scanned-WMS (right panel) laser absorption measurements (black) converted to dry basis mole fractions compared with GC (blue) and FTIR (red) data.

Figure 6.1 Mid to low current conditions at Disk 4. The 2 atm condition is the lower temperature limit for the sensor. The data in black represent three separate runs at the same conditions.

Figure 6.2 Maximum current conditions at Disk 4. Relatively flat temperature profiles indicate uniform flow.

Figure 6.3 CFD computation of temperature profile across the MV in the IHF. Temperature drops steeply near the wall.

Figure 6.4 Low to mid power (current) conditions at Disk 1. Add-air near the wall and low amperage conditions provide insufficient breakdown of oxygen at LOS D.

Figure 6.5 High energy conditions at Disk 1. High add-air case shows significant asymmetry. Although higher in amperage than the lower power cases, it is still not sufficient to see atomic oxygen at LOS D.
**Figure 6.6** Maximum power cases. High add-air condition at Disk 1 shows unstable temperature profile.

**Figure 6.7** Centerline LOS measurements. High add-air cases show significant temperature drop.

**Figure 6.8** Time resolved temperature measurements during a single run in the IHF. The arc-off shutdown transient is evidenced by the sharp drop in temperature.

**Figure 6.9** Centerline enthalpies based on the temperature data shown in Figure 6.7. Amount of add-air significantly impacts the cooling at Disks 1 and 2. Sonic throat and energy balance enthalpy measurements are included as well. The black dashed line indicates the approximate location of the nozzle entrance.

**Figure 8.1** Photo of the interior of the arc column. Three LOS are indicated by the red dots on Disk 1. Flow here is right to left.

**Figure A.1** Baseline ($I_o$) intensity in red, and ($I$) and transmission intensity during an IHF run. Baseline intensity is recorded while arc heater is off.

**Figure A.2** Major components in the New Focus TLB-6900 ECDL. The ECDL implements a Littman-Metcalf laser cavity system.
1. Introduction

1.1 Renewable Energy Resources

The gasification of biomass waste and subsequent processing into synthetic natural gas offers an untapped potential energy resource, especially from the large amount of available agricultural waste materials.[3] The production of synthetic natural gas from agricultural waste gasification could be more efficient if the hot, pressurized gasifier output was directed immediately into a synthetic natural gas production reactor. Unfortunately, typical gasifier output streams can vary in time and efficient synthetic natural gas production requires a stable composition of the gasifier output stream. If commercial synthetic natural gas production is to be realized from agricultural waste gasification, real-time gasifier control is required. Hence, sensors providing real-time analysis of the gasifier product composition with sufficient time resolution for gasifier process control are needed. For current synthetic natural gas production, real-time knowledge of the H$_2$O mole fraction of the biomass gasifier product stream is especially important because the natural gas production relies on the water-gas shift chemistry; real-time knowledge of the water vapor content of the fuel stream is needed to control the optimum steam addition to the natural gas production reactor.

Typical instrumentation methods used to monitor producer gas from gasification of coal or biomass use standard analytic chemistry tools such as gas chromatography (GC) and Fourier transform infrared (FTIR) spectrometers. For the gasifier in this study,
typical product stream composition is made up of H₂O, CH₄, CO₂, CO, and H₂. Here producer gas is defined as the gas products that result from steam gasification. Mention of gasification in this body of work refers to steam gasification. Both of these monitoring tools require conditioning of the gas, filtering any particulate, and removing the water vapor (drying) from the gas. This conditioning limits the response time. Rapid changes in composition can be smoothed in time by diffusion in the gas conditioning filters and driers.[4] Also, water vapor is an important component in producer gas. For example, excess water provides the operator with an important indicator of the health of bed material for fluidized bed gasifiers. In addition, if the producer gas will be used to produce synthetic fuels, the nascent H₂O content of the producer gas is needed to understand the optimum steam to add for Fisher-Tropsch conversion.[5]

In situ laser absorption sensing provides a solution to the needed sensor for biomass gasification products, especially when the H₂O content is important. Typically, an absorption sensor determines gas composition and flow properties from a measurement of the fractional transmission of laser intensity as a function of laser wavelength; when the laser is tuned to a wavelength in resonance with an absorption transition the transmitted intensity reaches a minimum.

Laser absorption sensors have a long history for in situ combustion sensing.[6]–[8] Important work has also been reported for gasifier applications. Lackner et al. [9] monitored C₂H₄ with mid-infrared (MIR) scanned-direct absorption spectroscopy (DAS) in biogas at 1 atm in a room temperature cell. Recently, Nau et al. used MIR to
monitor CO, CH₄, and H₂O in a two-stage gasifier similar to the one used here for biomass.[10] Separately, diode laser absorption sensing was used to detect HCl emissions in producer gas from biomass gasification.[11] Other laser-based diagnostics have also been successful in gasifier product gas, e.g. Karellas and Karl [12] used Raman spectroscopy to monitor the composition of producer gas identifying the specific species H₂, CO, CO₂, CH₄, and H₂O and non-selectively monitoring the large hydrocarbon tars in the flow. At Stanford there has been a significant effort to develop laser absorption sensing for sensing of coal gasification products. Sun et al. [13], [14] used fixed-wavelength modulation spectroscopy (WMS) to monitor H₂O, CO, and CO₂ in product stream from a high-pressure entrained-flow coal gasifier. This work was extended to scanned-WMS [15] in the producer gas from an industrial-scale fluidized-bed coal gasifier, and further extended to CO, CO₂, CH₄ and H₂O in the same gasifier.[4] Here efforts were taken to develop and provide a proof-of-concept demonstration for quantitative, *in situ*, time-resolved monitors of H₂O, CO, CO₂, and CH₄ in the product stream from a pilot-scale biomass gasifier. This prototype sensor used only readily available lasers in the telecommunications bands in the near-infrared region of the spectrum (1350-1680 nm), and the sensor was designed to provide the time resolution needed to efficiently control and optimize the biomass gasification process.

Wavelength selection to optimize sensor performance for the specific application is an important part of the design. A prototype sensor was then constructed and laboratory tested in gas mixtures at known temperature and pressure to validate sensor performance. Field measurements were then conducted in a pilot scale biomass
gasifier at West Biofuels in Woodland, California. Two techniques for laser absorption sensing are investigated here: scanned-DAS and scanned-WMS. Although scanned-DAS is simpler to implement and interpret the resulting data, scanned-WMS offers noise rejection and reduced complications in measurements with non-absorption transmission losses due to particulate scattering and beam steering. The level of particulate scattering in the producer gas where measurements were expected to be made were unknown. Thus, it was anticipated that a scanned-WMS laser absorption sensor would have improved performance in producer gas from biomass gasification, a gas flow typically laden with tars and solid particulate. The relevance in using scanned-WMS to mitigate for tars is due to the fact that when allowed to cool, the tars would condense on the optical access windows and overtime deposit an opaque layer of tar on the windows. Scanned-WMS also has the added advantages for real-time analysis for process control sensors.[16]
1.1.1 Biomass Gasifier

A pilot-scale, fast-circulating, fluidized-bed gasifier operated by West Biofuels in collaboration with the team from the University of California San Diego was the field test target of the diode laser absorption sensor development. The gasifier is based on the successful commercial design used to produce bio-diesel and heat from wood chips.\[1\], [2] The gasifier is fueled via a screw auger loaded with biomass pellets made from organic almond waste. As shown in Figure 1.1, the two-stage process first uses steam on the gasification side to drive the volatiles (roughly 70%) from the biomass into the producer gas. The remainder of the biomass is consumed on the combustion side where air is injected and the char is combusted thereby heating the bed material. Auxiliary fuel (propane) is sometimes use in the transient startup process of the plant to initiate the gasification cycle. The flue gas and bed material are separated using a cyclone and re-introduced back into the gasification chamber.\[17\] The West Biofuels gasifier investigated in this study is a 1 MWth, with capacity of 6 tons of biomass per day. Further details including simulations and specific details of this pilot scale gasifier are provided by Liu et al.\[18\], [19]

The bed material plays an important role in the long-term commercial viability of biomass gasification as an alternative renewable energy resource. In the past, commercially available bed material like CARBO ceramics have been used.\[2\] At the time of the study, a high performance Ni-Fe-Mg bed material was under investigation.\[20\] The bed material is used to transfer heat to the biomass fuel for conversion into char. This multi-species sensor was able to identify opportunities in the
gasification process to help reduce degradation of the bed material. The benefit to the quality of the bed material is explained further in the field-test results section below. In addition to the bed material’s effects on H\textsubscript{2} gas yields and reduced tar concentrations,[21]–[23] the quality of the bed material is largely correlated to the overall cost involved in operating a bio-syngas fast-internally-circulating fluidized bed gasifier like the one studied at WestBioFuels. WestBiofuels has experimented with many bed materials to improve gasifier performance. Degradation of the bed material reduces its lifetime and increases the maintenance and downtime costs associated with replenishment of new bed material. This sensor therefore becomes a valuable tool in helping to indirectly monitor the health of the bed material in real-time.

**Figure 1.1** (a) Sketch of the fast circulation fluidized bed biomass gasifier at West Biofuels where red arrows show the biomass input, blue the steam input, cyan the air input, green the producer gas output, and orange the flue gas exhaust. The bed material is illustrated by the black dots. (b) Photo of the pilot-scale gasifier illustrating flow paths with the same arrow color code. Further details on the gasification process can be found in.[1], [2]
The producer gas from this research gasifier gets directed to a small analytic chemistry laboratory for analysis and used to study gasifier performance. The biomass gasification work described here will focus on the design and construction of a sensor for real time monitoring of H₂O, CH₄, CO₂, and CO in the producer gas product stream. For these proof-of-concept measurements in the producer gas output of the West Biofuels gasifier, direct comparison with the analysis in the analytic chemistry laboratory was important. The location of the flow cell was installed so as to draw flow directly from the producer gas pipe just before entering the chemistry laboratory as illustrated in Figure 1.2.

The sensor installation in the West Biofuels gasifier, illustrated in Figure 1.2, is located approximately 15 m downstream of the gasifier, just prior to the tar reformer (at this location the producer gas pressure was approximately atmospheric). The valves shown in the figure allow the producer gas flow to be diverted through the 1 m optical sensor path for laser-absorption measurements. This design provides an optical measurement cell of flowing producer gas where the time resolution is limited by the residence time of the gas between the two optical ports (2 seconds for the typical operation of the West Biofuels gasifier). The valves and purge flows allow the producer gas to bypass the optical sensor cell in the event the optical ports required cleaning or other optical cell maintenance or allow the measurement of a non-absorbing signal for sensor setup and testing. For a scanned-WMS type sensor, this non-absorbing signal (cell is filled with nitrogen gas) is used to calculate the background \( \frac{2f}{1f} \) signal. For all the sensor measurements conducted during this study, no optical cell maintenance was needed and no window fouling was observed. This is credited to maintaining the cell at
an elevated temperature. Although not shown in the figure, the gas flow and optical cell is encased in a custom heating jacket (HTS/Amptek), which maintains the producer gas, the cell, and its windows at constant temperature, ~120° C. Accumulation of tars on the optical windows was prevented by flowing nitrogen through the optical cell after every test campaign.

**Figure 1.2** Absorption cell flow path for the West Biofuels gasifier with temperature controlled plumbing to match the producer gas line. The entire producer gas stream is diverted through the cell for laser absorption measurements of H₂O, CH₄, CO₂, and CO.
1.2 Advanced Thermal Protection Systems

Advanced thermal protection systems (TPS) are critical to enabling exploration to and from other planets and celestial bodies in our solar system. Adequate testing of TPS materials requires extreme temperatures and pressures to recreate the high-enthalpy atmospheric entry conditions encountered by spacecraft.\[24\]–[27] Using various diagnostic methods, Park et al. showed that the Interaction Heating Facility (IHF) can generate a supersonic flow of arc-heated air plasma having centerline enthalpies downstream of the nozzle up to 30-40 MJ/kg.\[28\] The focus of this study was to expand sensing capabilities and better understand the mixing between the add-air flow and the main flow in the 60 MW Interaction Heating Facility (IHF) at NASA Ames Research Center. The IHF is relied upon for TPS flight and materials testing.\[29\]–[31] To help simulate the various atmospheric flight profiles encountered by spacecraft in a ground-based facility, ambient air (add-air) is injected into the arc-heated main gas stream in the subsonic section upstream of a converging-diverging nozzle of the IHF. Figure 1.3 illustrates the mixing volume (MV) located immediately downstream of the arc-heater. Any reference to temperature and pressure refers to the temperature and pressure of the flow in the MV unless otherwise specified. Add-air injection provides tunability of the heat flux and stagnation pressures generated at the exit of the nozzle by decreasing the bulk enthalpy of the flow of test gases that enter the nozzle. However, direct add-air injection can add to the radial non-uniform temperature profiles of the flow generated by the plasma arc heater.\[32\] Without sufficient mixing length, unmixed regions of the flow result in non-uniform heat flux and stagnation pressure profiles applied to the TPS test
models downstream of the nozzle exit, making it difficult to achieve predictable and repeatable test conditions.

To facilitate mixing, a MV was installed immediately upstream of the nozzle inlet, as pictured in Figure 1.3 in two views; axial and radial cross-sections of the MV. Plasma flow exits the arc heater portion and enters the MV (internal diameter $= 12$ cm, length $= 51$ cm) from the left side where pressurized ambient air (add-air) is injected along the walls of the MV. Mixed air and plasma flow enter the convergent-divergent nozzle and exit on the right to impinge on a TPS sample (not shown) inside an evacuated chamber. Further details of the facility, including the add-air configuration before and after the addition of the MV, are described by Nations et al. [32, 33]

![Figure 1.3](image.png)

**Figure 1.3** Add-air mixing volume consists of add-air, optical, and spacer disks. A typical optical disk is shown in the downstream view. Line-of-sight B is located at the centerline.

The MV is made up of add-air injection, optical, and spacer disks stacked sequentially. This stack of disks is what creates the main flow path. All are water cooled to manage the arc-generated heat load. Previous research efforts reported by Nations et
al.[33] demonstrated improved mixing after installation of the MV. For a pressure of 1.8 atm, it was demonstrated that for add/main air mass-flow ratios of 0.27 and 0.93, installation of the MV yielded relatively flat temperature profiles across the flow.[33] Add/main ratios refer to the ratio of add-air mass flow to main flow mass flow. This provided uniform flow for these particular high add-air conditions that had been non-uniform prior to installation of the MV. Optical access is obtained in either of the four disks as shown in Figure 1.3. These measurements were made at Disk 4, which is located at a length-to-diameter ratio of L/D = 2.1, downstream of add-air injection. For reference, the MV is located 0.7 diameters downstream of Disk 4.

The extreme temperatures, typically between 5,000 – 8,000 K, within the MV gas stream require significant water cooling. The addition of the MV improved uniformity of the flow upstream of the nozzle inlet (Disk 4) due to the increased mixing length but resulted in approximately a 20% reduction in the maximum achievable centerline enthalpy of the IHF. Even in the absence of add-air injection, introduction of the MV yielded significant heat loss to the walls and thus a reduction in the overall enthalpy of the flow. Since high enthalpy and uniform flow capabilities are both critical to IHF customer needs, this study was focused on understanding how add-air injection contributes to line-of-sight (LOS) uniformity. Measurements made in this study were aimed at gaining a better understanding about the axial distance in the MV beyond which additional mixing volume length no longer provides improved mixing but rather, results only in heat loss to the walls. The potential here is that by optimizing the mixing process and reducing the length of the MV, enthalpy losses could be recaptured and restored to the levels observed prior to installation of the MV.
For this IHF sensing study, a scanned-direct absorption spectroscopy (DAS) sensing strategy was implemented. The IHF environment is extreme and has limited optical access. Although beam steering can be problematic, especially when optical access is this limited (optical diameter is 3 mm), the optical path can be engineered to mitigate some of the beam steering effects. While scanned-WMS would have been a more suitable candidate, the external cavity diode laser available for this study was not capable of tuning at the modulation frequencies needed for scanned-WMS. Implementation of scanned-WMS in the IHF is discussed further in the future work chapter below.

Another benefit of implementing scanned-WMS is that because of the high temperature nature of the test gas in the IHF, it makes calibration via other sensing methods impractical and prohibitively expensive. The non-calibration nature of scanned-DAS and the access to fiber coupling of the system makes it a suitable candidate for this environment. In addition to temperature sensing, implementation of scanned-DAS has the added benefit of quantifying bulk and centerline enthalpy of the IHF. The key point here is that the proportionality of enthalpy to heat flux makes the former a thermodynamic parameter of interest to arcjet test campaigns. A significant motivation for improving enthalpy sensing is the direct correlation between enthalpy uncertainty and TPS performance. In some previous cases, the TPS mass fraction has accounted for up to 70% of the total entry vehicle mass fraction, thereby significantly reducing payload capabilities.[25] Non-intrusive and direct measures of enthalpy in an arcjet have been a topic of study for some time, [34]–[36], especially in the cases where non-equilibrium flow exists. It requires knowledge of the ionized components of a gas stream that is costly.
to recreate. Park et al. provide a comprehensive review of the conventional methods used in determining arcjet-generated enthalpies, including a non-intrusive method.[28] In the following opportunities for a recapture of enthalpy loss to the walls and an improved determination of centerline enthalpy within the MV of the IHF arcjet are demonstrated.

The sensor improvements achieved in this study widened sensing capabilities. The increased capability of the sensor allowed for sensing at much higher pressures and lower temperatures than had been measured previously, while simultaneously reducing the overall uncertainty of the measurements. This in turn allowed for an increased understanding of the axial temperature profiles of the flow within the MV, thereby providing an opportunity to develop new add-air injection schemes to optimize the add-air mixing process and recapture the maximum enthalpy capabilities that were lost due to installation of the MV.
2. Absorption Spectroscopy Theory and Techniques

2.1 Absorption Spectroscopy Theory

The foundation of the laser diagnostic techniques implemented in sensor development fundamentally revolves around light-matter interaction. In many of the applications under consideration in remote sensing, scattering and reflected light can be neglected. This leaves absorbed and transmitted light as the two forms of interaction of interest. By combining classical radiative transfer with the Einstein Theory of Radiation and an appropriate lineshape model for the allowed transitions of interest, one can derive Beer’s Law into a form relevant to the applications considered in this study. Equation 2.1 contains a relevant form where $\alpha$ is the absorbance, $I$ and $I_o$ are the transmitted and baseline intensity, respectively, $S$ is the species-dependent lineshape of the transition being investigated, $\phi_\nu$ is a frequency-dependent lineshape function, $P$ is pressure, $x_i$ is the mole fraction of the species under investigation, and $L$ is the pathlength (assumed uniform) over which the gas absorbs the incident laser light.

A full derivation of the various forms of Beer’s Law can be found in [37]. However, it is important to mention the assumptions that are made in deriving this form of Beer’s Law. In this radiative model, reflection and scattering are assumed to be negligible and is only valid in the optically thin limit. Additionally, the spontaneous emission term in the radiative model used for the derivation of Equation 2.1 is omitted.

$$\alpha_\nu = \left(\frac{1}{I_o}\right)_\nu = \exp \left(-S_\nu\phi_\nu P x_i L\right)$$

Eq. 2.1
The form of Equation 2.1 can vary and is largely dependent on the availability of spectroscopic data for the species under investigation. For polyatomic molecules relevant to combustion applications, for example, extensive databases provide the necessary spectroscopic data needed to fully model the absorption behavior of those species. Specifically, linecenter, Einstein coefficients, and collisional widths of H$_2$O, CO, CO$_2$, and CH$_4$ are provided, just to name a few. Databases like Spectraplot[38] and HITRAN[39] have enabled quick modeling tools that are readily available and allow for modeling of the gas environment under consideration. For example, in the design of the biomass gasification sensor, all of the species under investigation absorb in the infrared. The modeling described in the multi-species section below is important and insightful in finding narrow regions in wavelength space where one species absorbs and all the others have absent or negligible absorbance. As Zhou et al. show, careful and systematic modeling is critical for developing optimized diode laser-based diagnostics.[40]

The sensor design process for atomic oxygen is a much different process than for the common diatomic polyatomic species relevant to combustion. It illustrates how much the availability of spectroscopic data affects the design process. For example, the inherently extreme environment of the IHF makes it incredibly difficult to re-create the necessary conditions for a prolonged enough amount of time to experimentally validate linestrength. However, in a typical sensor design process like the one implemented for the biomass gasification sensor, a gas cell can be used to combine room temperature gases of interest. Figure 2.1 is a photo of this type of measurement cell. Known quantities of the species of interest were flowed through the cell to validate the sensor.
The flow cell in Figure 2.1 is the same flow cell illustrated in Figure 1.2. Depending on which valves are open and closed, the flow through the cell is either a known mixture of gases or a producer gas flow.

Figure 2.1 The gas flow cell used to make measurements at WestBiofuels was also used as a reference cell. It allowed for spectroscopy measurements that validated fundamental spectroscopic parameters including linestrength. It also validated the multi-species sensor measurements by flowing known flow quantities of the species under investigation.
Due to the fact that linecenter and linestrength are fundamental parameters, the data needed to calculate linestrength for example, can be collected by using gases at room temperature and near-atmospheric pressures. The measured fundamental properties of the gas can then be used for applications at higher temperatures. However, a reference cell for atomic oxygen is much more complex and limiting. Figure 2.2 contains a photo of a reference cell used for studying atomic oxygen. This discharge cell was used to identify the location of the atomic oxygen transition, in wavelength space, relative to the output of the laser head. The output power for this system is a function of the fixed and variable voltage applied to the piezoelectric motor that is used to mechanically tune the optical components within the ECDL laser system. More about the specifics of how the laser is operated can be found in Appendix A.

Figure 2.2 Reference cell used for calibrating atomic oxygen sensor with respect to transition linecenter. This type of cell requires a high-power radio frequency source and is limiting in terms of the quantitative value that it can provide.
2.2 Scanned-Direct Absorption Spectroscopy

Scanned-DAS has been implemented in a variety of gas sensing applications for many decades.[41]–[49] It is a valuable tool when the broadening parameters for the environment under investigation are unknown due to either a lack of data in the literature or when many species make up the gas and measuring them directly in laboratory setting is time or cost prohibitive. For example, the HITRAN databases [50] contain self-broadening parameters for many species and the corresponding collisional broadening parameters for nitrogen and oxygen in air. Contributions from minor species are neglected. Although this allows for quite a large set of gas compositions, it quickly becomes evident that many gas-dynamic systems of interest require known values of these spectroscopic parameters or that an alternative is needed. One alternative is scanned-DAS.

In both the biomass gasification and atomic oxygen sensing studies scanned-DAS was implemented. A fixed-DAS approach, although simpler in implementation, would have required a prohibitively timely and costly evaluation of the broadening parameters of the collisional partners. In the biomass gasification case, it was a matter of time and cost of mitigating for toxic (e.g. CO) and caustic (e.g. H₂S) gases. The chemical makeup of ionized air in the IHF arc heater is complex with limited knowledge of the spectroscopic parameters. Scanned-DAS is a readily available method for developing a diagnostic when temporal measurement resolution is not a major factor, as is the case with many shock tube kinetic studies.[51] Such studies attempt to monitor gas properties
on microsecond timescales and thus would not allow for the often lengthy timescales required to scan a laser across a single transition.

By scanning, in wavelength space, across the transition of interest, an absorption model can be used to fit the measured absorbance profile. By tuning the spectroscopic parameters of the model, the area under the measured absorbance profile can be calculated and used in a Beer’s Law formulation like Equation 2.1 to calculate the unknown parameter, e.g. mole fraction. By resolving the absorbance profile in its entirety, the collisional broadening parameter problem is entirely avoided. This has the added benefit of not having to know the overall composition of the gas. Only the composition of the species under investigation is needed.

Problems can arise, however, in the tuning capabilities of the laser being used. Optimization of the sensor used in the IHF to overcome this problem is described below. Although scanned-DAS provides benefits and is an improvement over fixed-DAS, especially for the biomass gasification and atomic oxygen sensing applications, it is limited and can be susceptible to reduced signal quality in environments with high mechano-vibrational noise and/or high amounts of radiative emission.
2.3 Scanned-Direct Wavelength Modulation Absorption Spectroscopy

The implementation of and the details around scanned-WMS are not provided here since it has described in detail in the literature,[16], [52], [53] It is not the intent of this body of work to add to the scanned-WMS technique, beyond what is described in Section 3.2. Instead scanned-WMS is discussed in this section with the intent to describe the implications of developing a sensor for the two applications that were investigated, biomass gasification and atomic oxygen detection.

The scanned-WMS technique employed in this body of work applies only to the biomass gasification sensing. Due to the large number of target transitions that were under investigation, a time-multiplexed technique was implemented in order to prevent potential crosstalk among the various harmonics from all five lasers. This provided the benefit of not having to choose the modulation frequency based on this type of interference. The choice of modulation frequency was instead driven by the increasingly non-linear response of the lasers to high-frequency modulation. Unique insight into the development of scanned-WMS and guidelines for avoiding the deleterious effects of the non-linear response of diode lasers to high modulation frequencies is provided in Section 3.2.
2.4 Single-Line Thermometry

The IHF conditions investigated in this study differ from the majority of gas sensing applications, *i.e.* sensing of combustion chemistry-related molecules, in that the gas under investigation is highly energized and decomposed air. The primary components of the gas in the MV of the IHF are N$_2$, N, and O. There is a minor amount of Ar in the system, although it has no significant effect on the design and implementation of the sensor. Atomic oxygen’s triplet transition near 777 nm was chosen due to the availability of high-power diode lasers in that wavelength region. The external cavity diode laser that was chosen allowed for fiber coupling and lent itself to field deployment for *in situ* sensing.

The following is a brief description of the scanned-DAS method as it was adapted to a single-line thermometry technique. Details of the spectroscopic parameters used for this particular atomic oxygen transition are given by Nations *et al.*[32] An iterative single-line thermometry approach was implemented in order to solve for the electronic temperature of atomic oxygen. Thermal-chemical equilibrium, and thus local thermodynamic equilibrium (LTE), was assumed due to the high pressures of the system under investigation, 1-9 atm. Since thermal-chemical equilibrium is assumed, a single temperature $T$ in Equations 2.2-2.4 is used. Since the gas is assumed to be in thermal equilibrium, the electronic temperature that is solved for in measuring the atomic oxygen transition of interest is the thermal equilibrium temperature $T$ of the gas. Atomic oxygen number density, $n_o$, the lower state number density of the transition, $n_l$, and the Boltzmann fraction are the key relations used in iterating toward convergence of the
temperature of the gas. Equations 2.2-2.4 describe the process of arriving at a solution for temperature.

\[
n_o = \frac{p x_o}{k_b T} \quad \text{Eq. 2.2}
\]

\[
n_l = \frac{A_{int}}{SL} \quad \text{Eq. 2.3}
\]

\[
\frac{n_l}{n_o} = \frac{g_l}{Q} e^{-\left(\frac{E_l}{k_b T}\right)} \quad \text{Eq. 2.4}
\]

The IHF’s pressure transducers provide a known pressure, \( p \) (e.g. 8 atm), within the MV. Assuming an initial LOS temperature, \( T \), (e.g. 7,000 K) allows calculation of the corresponding chemical equilibrium atomic oxygen mole fraction for that given thermodynamic state at \( T \) and \( p \). The initial temperature is assumed based on the historical data of the condition that is set in the IHF. The equilibrium calculation is conducted through Matlab using the Cantera equilibrate tool.[54] Number density, \( n_o \), of atomic oxygen is then calculated using Equation 2.2., where \( k_b \) is the Boltzmann constant. \( S \) and \( L \) in Equation 2.3 are the transition linestrength and the LOS path length, respectively. \( A_{int} \) is the integrated absorbance and is determined experimentally through a least-squares Voigt fit of the experimentally measured absorbance. Figure 2.3 contains one of these fits, shown at a condition that was not attainable prior to this study due to the relatively high level of injected add-air. More about the details of this condition are described in the results section below.
Experimentally measured and Voigt fit absorbance profile of an atomic oxygen transition. At the pressure shown, $P = 4.1$ atm, the laser must be scanned at least over a range of at least $2 \text{ cm}^{-1}$ in order to accurately calculate the integrated area of the transition that is needed to infer temperature.

Once the atomic oxygen and lower state number densities are known, the Boltzmann fraction (Equation 2.4) can be used to solve for $T$. The initial guess for $T$ in Equation 2.2 is compared with the calculated value of $T$ in Equation 2.4. If the temperatures vary considerably, then the calculated $T$ value from Equation 2.4 is used as the new estimated value for $T$ in Equation 2.2. This iterative cycle continues until the values converge to within 10 K, normally, within 2-4 iterations. Setting the convergence limit to anything less than 10 K results in a negligible difference between the results and requires many more iterations. The average uncertainty for the condition shown in Figure 2.3 is $\pm 65$ K. This is exceptional given the extremely high level of add/main ratio.

It is important to note that while the uncertainty based on the fit is low, it should be weighed against the assumptions made in arriving at the calculated value of $T$. 

Figure 2.3
Thermal equilibrium is the major assumption to consider. It is likely that due to the high pressures in the MV, this assumption is in fact valid. However, past efforts by Nations et al.[55] indicate non-equilibrium conditions for atomic oxygen at lower pressures.

Potential future work to explore at which conditions the thermal equilibrium assumption begins to breakdown is discussed further in the future work chapter.
3. Multi-Species Sensor Design

3.1 Design and Implementation

Data from GC and FTIR spectrometer measurements were gathered and nominal values are those reported in Table 3.1. These data are the basis for the modeling of the absorption spectra and the starting point for the line selection process. Knowing the typical gas composition, temperature, pressure, and optical path length, absorption spectra of the producer gas can be predicted to optimize the laser absorption sensor design. In this study typical conditions were 300K-400K, 1 atm, and the pathlength was 1m. For the measurements made in this study, the gasifier feed consisted pellets made from almond pruning.

<table>
<thead>
<tr>
<th>Species</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.33</td>
</tr>
<tr>
<td>CO</td>
<td>0.30</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.20</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.10</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.07</td>
</tr>
</tbody>
</table>

**Table 3.1** Mole fraction of major species in producer gas products of biomass gasification.
Careful selection of absorption transitions is an important part of the design of a laser absorption sensor. If the gas composition, pressure, and temperature is known or a range of these values can be estimated, the sensor designer can calculate an absorption spectrum of the gas. Once the absorption spectrum is known, the strength of the laser absorption signal only requires an estimate of the path length in the gas flow where a sensor can be installed. Not only must the selected transition have sufficient absorption signal for detection, but species selective monitoring requires that only one species in the gas mixture absorb at the target wavelength. Except for H₂, all of the other major species in the producer gas mixture in Table 3.1 have rich and relatively strong absorption spectra in the near-infrared with active overtone and combination band ro-vibrational transitions. Thus, the target species (CH₄, CO, CO₂ and H₂O) can be monitored by near-infrared laser absorption. Knowledge of the mole fraction for these four species and the assumption of H₂ as the gas balance along with the good understanding of the carbon content of the fuel, provides sufficient knowledge of the H₂ mole fraction for control of the gasifier and/or the subsequent synthetic natural gas production. The WestBiofuels gasifier has used commercially available pellets of different kinds which can vary in composition.[2] Almond pruning for example, which is what was used during this study, has about 51% C content.[56]

A laser absorption sensor for the four target species showing four multiplexed lasers is illustrated in Figure 3.1. Laser light is directed through the target gas mixture and the intensity is attenuated by absorption as the laser wavelength is tuned to match the wavelength of an absorption transition. The absorbance is given by Beer’s Law as described above in Equation 2.1, where the transmitted intensity $I_t$ of narrow-bandwidth
light source of incident intensity $I_0$, as it passes through a uniform absorbing medium. Upon integration over frequency space, the integrated area of the transition can be expressed by Equation 3.1. This form of integrated area allows for an explicit solution of mole fraction when the temperature and pressure of the gas are known.

$$A_{\text{int}} = S_i(T) P x_i L$$  \hspace{1cm} \text{Eq. 3.1}

**Figure 3.1** Four lasers, one for each target species in the gas mixture, are combined on an optical fiber (wavelength division multiplexer), collimated into a free-space beam and directed through a gas mixture. The transmitted light is collected and focused onto a detector. The laser controller time-multiplexes the four lasers, so that only one laser is operating at a time, and sequential measurements are made at rate of 50 Hz.

Computational prediction of the absorption spectrum requires specification of absorbance as function of laser wavelength. This requires for each chemical species in the gas mixture, a line list of absorption transitions providing wavelength, line strength, and collision-broadening information. Such data are available in the HITRAN database.
[39] for common combustion gas species including H$_2$O, CH$_4$, CO$_2$, and CO. This spectral model is used to predict the absorption spectrum for producer gas with the composition as given in Table 3.1, providing an absorbance spectrum for the producer gas mixture (absorbance versus laser wavelength). These simulations assumed atmospheric pressure and 120 °C, which are the current producer gas output conditions of the West Biofuels pilot-scale biomass gasifier.

Once the absorption spectrum for producer gas is known, candidate wavelengths can be selected for a prototype sensor. The goal here is to select laser wavelengths that are sufficiently absorbed by the gas to make sensitive measurements of the target species mole fraction, while noting that if the absorbance becomes too large a transition becomes optically thick (here it is defined as $\alpha > 2$) and sensitive measurements are not possible. Thus, one of the design rules is to select transitions with absorbance between 0.1 and 2 (laser transmission between 90% and 10%). A second goal is to select laser wavelengths that are only absorbed by the target gas and do not have interference absorption by other components of the gas. These two sensor design goals combined with various noise sources suggest design rules for selecting the optimal sensor wavelengths.[57] Using such design rules, numerous candidate laser wavelengths are available in the telecommunications region for detection of H$_2$O, CH$_4$, CO$_2$, and CO assuming an optical path of 1 m. Thus, for the prototype sensor, it was possible to choose transitions that were accessible with already available lasers. The absorption spectrum of producer gas with the composition of Table 3.1 was simulated with the HITRAN database [39] and the regions around the wavelengths selected for the sensor are illustrated in Figure 3.2. The temperature dependence of the selected transitions is
illustrated by plots at 300 K, 350 K, and 400K for a 1 m path length at 1 atm pressure. Note the selected transitions near 7203.9 cm\(^{-1}\) (1388.1 nm) for H\(_2\)O, 6047.0 cm\(^{-1}\) (1653.7 nm) for CH\(_4\), 6243.8 cm\(^{-1}\) (1601.6 nm) for CO\(_2\), and 6383.1 cm\(^{-1}\) (1566.7 nm) for CO have only very small interference from the other major species in the producer gas mixture.

Figure 3.2 Simulations at 300, 350, and 400K for the absorption spectrum of producer gas at 1atm for a 1m path length in the region of the wavelengths selected for the sensor, where H\(_2\)O, CH\(_4\), CO\(_2\) and CO can be selectively monitored.

A prototype laser absorption sensor was assembled as per Figure 3.1 using standard distributed feedback (DFB) telecommunications fiber-coupled tunable diode lasers. The lasers used to monitor CO and CO\(_2\) were manufactured by CyOptics and emitted light with approximately 5 mW of power. The lasers used to monitor H\(_2\)O and
CH₄ were manufactured by NTT Electronics Corporation and emitted light with approximately 10 mW of power. The light from the four lasers was multiplexed onto a single fiber with a 4x1 fiber combiner. The laser light exiting the fiber was collimated into a free space beam with ~1 mm diameter. For the validation experiments in the laboratory this light was directed through a gas cell containing gases of known temperature, pressure, and composition; and for the field measurements this light was directed through the laser absorption fixture. The transmitted light was collected with a 25 mm diameter free space lens (25 mm focal length) and focused onto a PDA10CS (Thor Labs) InGaAs detector with an operating range between 900-1700 nm, an active area of 0.8 mm², and a 17 MHz bandwidth. The detector signal was digitized (National Instruments PXI-6115) and the time-resolved laser intensity measurements collected.

A synchronized analog waveform was used to drive the injection current of the four lasers. The laser wavelength was injection-current scanned for scanned-DAS and modulated in addition to being scanned for scanned-WMS using commercial laser control power supplies (ILX). This meant that the commercial controller set points for DAS and WMS were different. The analog output waveform was used to time-multiplex the four lasers so that each laser is activated in turn for 5 ms as illustrated in Figure 3.3. A complete set of four measurements was completed every 20 ms for a measurement rate of 50 Hz. The scan frequency for all four lasers was 400 Hz and the modulation frequencies for H₂O, CH₄, CO₂, and CO were 100, 100, 40, and 50 kHz, respectively.
The variable gas composition of the producer gas products from the biomass gasifier leads to the need for scanned-wavelength approaches of laser absorption, which can be used to infer integrated absorbance. Quantitative absorption spectroscopy measurements of mole fraction by fixed-wavelength approaches require knowledge of the collision-broadened line shape. Unfortunately, the collision broadening varies with collision partner and thus varies with the gas mixture and is not known a-priori in the producer gas products. Scanned-wavelength approaches to absorption spectroscopy provide integrated absorption, which avoids this problem.

**Figure 3.3** Illustration of the time-multiplexed four laser sensor drive signals. Each laser is scanned for 5 ms on a 20 ms period. Each trace in the lower panel for DAS includes 0.25 ms of the scan below the laser threshold to obtain a thermal background measurement on the detector. The upper panel shows the drive signals for scanned WMS (modulated at 10 kHz).
Scanned-DAS is conducted by linearly scanning the laser wavelength (laser frequency) with a triangular waveform (yielding two measurements per 5 ms cycle). When the laser wavelength matches that of an absorption transition, the transmission is attenuated. Tuning the laser beyond the absorption feature allows the “baseline” or $I_0$ in Beer’s Law relation to be determined by extrapolation across the absorption feature. The resulting absorbance is then fit to a Voigt line shape to facilitate accurate integration as a function of laser wavelength. This integrated absorbance is then used with the linestrength, temperature measurement, and pressure measurement to determine the mole fraction of the target species. This relatively simple method of data reduction makes scanned-DAS quite powerful and often used to interpret laser absorption measurement data. The disadvantage of scanned-DAS is the need to measure or calculate the baseline intensity $I_0$. Many variables can make calculation of the baseline intensity problematic. Some examples are a non-linear laser intensity response to injection current, wavelength-dependent intensity variations (e.g., etalons from windows), noise sources at frequencies faster than the scan frequency, or low absorbance values ($\alpha < 5\%$).

Scanned-WMS adds a modulation waveform to the linear scan of the laser wavelength. Laser absorption information is now found in the transmitted intensity data at harmonics of the laser modulation frequency. These harmonics can be isolated using lock-in amplifiers to process transmitted intensity versus time data. WMS has previously been used to evaluate small absorbance signals as this method moves the data analysis away from the $1/f$ noise of dc-coupled measurements. The “background” of a WMS signal is near zero while the “baseline” of a DAS signal is that of the non-
absorbed laser intensity. Thus, WMS is essentially an absolute measurement while DAS is the difference between two relatively large numbers. Both of these issues, i.e. WMS’s background and DAS’s difference of large values, add noise to small signal evaluation. However, for harsh environments such as a gasifier, WMS has an important advantage; the signals can be normalized to account for non-absorption transmission losses (e.g., window fouling, scattering from particulate, long-term drift in the laser intensity). When the laser modulation simultaneously impresses modulation in both laser wavelength and laser intensity, as is the case for injection current-modulated diode lasers, the first harmonic of the modulation frequency becomes a measure of the zero absorption laser intensity, and can be used to normalize the second harmonic avoiding the need to determine a zero absorption baseline. Scanned-DAS can also account for non-absorption losses, however it is limited to fewer cases than are available with the $2f/1f$ scanned-WMS approach.

Wavelength-scanned-WMS was implemented and analyzed using the techniques described in detail in [16], [52], [53]. The absorption signal is extracted from the second-harmonic of the modulation frequency ($2f$), and then normalized by the first-harmonic signal ($1f$). The fundamentals of $1f$-normalized, $2f$-WMS were described in detail by Rieker et al. [16]. For the work described here, with large absorbances at the peak wavelength of the CH$_4$ and H$_2$O transitions, the $1f$ signal becomes quite small, producing large fluctuations in the $2f/1f$ signal. To mitigate this effect, an average $1f$ signal over the scan range was used for the normalization following the procedure described by Chang et al.[58] The scanned-WMS is fit with two free parameters (absorption linewidth and integrated absorbance);[53] thus, details of the collision
broadening do not need to be known, which is crucial to the producer gas monitoring where the gas composition is not known (hence the collision broadening is not known in advance). The details of wavelength-scanned-WMS and modern fitting methods are well described and the interested reader should turn to the references [16], [53].
3.2 Practical Considerations for WMS sensor design

The output frequency (wavelength) of diode lasers can be adjusted by varying the device temperature at fixed injection current or by varying the current at fixed temperature. Temperature change in the optical cavity results in the creation of a slightly different mode being created in the cavity, which in turn results in a slightly different output wavelength. Most convenient for sensor applications is to fix the temperature and scan or modulate the output frequency with injection current. Modulation at high frequencies however, can lead to non-linear laser response and negatively affect scanned-WMS sensor performance. If the laser response to injection current is perfectly linear, the transmitted intensity of the wavelength modulated light without loss will have zero signal at the second harmonic of the modulation frequency. However, there will be a non-absorption or “baseline” 2f signal if the frequency modulation is not linear. This baseline 2f signal, when put through a data reduction process, results in a mole fraction. Although this equivalent mole fraction can be accounted for and subtracted, it results in a higher sensitivity to any changes in the baseline intensity. The extent of the sensitivity is laser specific. This effect is captured by the data presented in the results section below.

Typically, the degree of non-linear response increases with modulation frequency, hence the laser has a larger baseline WMS-2f signal at higher modulation frequencies. For the sensor developed in this body of work, the non-linear response to injection current was more significant for the lasers used to monitor CO and CO$_2$ (CyOptics) versus those used to monitor H$_2$O and CH$_4$ (NTT). Table 3.2 compares the equivalent mole fraction for the WMS non-absorbing background signal for the lasers used for H$_2$O
and CO absorption at modulation frequencies of 25 and 50 kHz. Theoretically, the WMS non-absorbing background should have a zero $2f/1f$ signal and therefore a zero value for equivalent mole fraction. The non-linearity inherent to these lasers is what produces a $2f/1f$ signal and thus an equivalent mole fraction.

As expected, the non-linear response to injection current increases with increased modulation frequency. This is evidenced by the increased equivalent mole fraction with increased modulation frequency, illustrating that both laser devices have an increased non-linear response to injection current as modulation frequency increases. Note the linear response of the NTT laser produced an equivalent mole fraction on the order of 100 times lower than the CyOptics device.

This elicits two factors to consider for WMS sensor design. Firstly, diode lasers with nearly perfectly linear response to injection current are best suited for WMS sensing. Secondly, the non-linear response to injection current sets an upper limit to modulation frequency. The sensor cannot be designed with an arbitrarily high modulation frequency, although tempting due to the increased noise rejection benefits that come with increasing modulation frequency. Since there is a tendency for the background signal to change over time, the negative effects of a shifting WMS background on sensor performance can be reduced and potentially even neglected by calculating an equivalent mole fraction for a fixed modulation amplitude over a range of modulation frequencies, like the data presented in Table 3.2. The sensor designer can then choose a modulation frequency with a corresponding equivalent mole fraction that is negligible compared to the application for which the sensor is being designed. This will result in a reduced sensitivity of the sensor to changes in the baseline intensity of the lasers. Since the biogas measurements
presented in this study took place over a short period of time, (on the order of minutes) there was a negligible shift in the background signal. The equivalent CO mole fraction values shown in Table 3.2 however, would not be acceptable for a commercial application since it would require long-term monitoring of the product gas stream. The non-absorbing background signal could vary significantly over this period of time. Alternatively, the NTT lasers are well suited for most applications. Care however should be taken when choosing a laser. This point is made clearer in the laboratory results section. The key point being that it is critical for the sensor designer to characterize the non-absorbing $2f/1f$ behavior of the laser being used prior to commercialization or field implementation. In addition to evaluating the equivalent mole fraction of the laser being used, a measure of uncertainty that is independent of molecular cross section is provided in Table 3.2. After accounting for the high absorbances due to water by multiplying with the integrated area $A_{int}$, the value for CO is much lower. This illustrates the high value of integrated area that $H_2O$ has over CO due to the high absorbance of $H_2O$.

<table>
<thead>
<tr>
<th></th>
<th>$x_i$ at 25 kHz</th>
<th>$x_i$ at 50 kHz</th>
<th>$A_{int} \times$ FWHM (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td>0.0069</td>
<td>0.0189</td>
<td>0.016</td>
</tr>
<tr>
<td>$CO$</td>
<td>0.45</td>
<td>0.75</td>
<td>0.0017</td>
</tr>
</tbody>
</table>

**Table 3.2** Equivalent mole fraction of $2f/1f$ non-absorbing background signal and a cross-section independent measure of uncertainty. As expected, equivalent mole fraction increases with increased modulation frequency. Although the high equivalent mole fraction values for CO can be subtracted and accounted for, it results in a high sensitivity to changes in scanned-WMS background, which leads to reduced sensor performance.
As an aside, there will also be a non-zero absorption $2f$ signal in the transmitted intensity if the transmitted light has other wavelength-dependent losses over the modulation amplitude (for example etalons associated with windows or other transmission optics). Thus, WMS laser absorption sensors must be optimized to minimize any non-absorption WMS background; note that etalon response can be reduced with anti-reflection coated optics and careful beam alignment.
4 Atomic Oxygen Sensor Optimization

Figure 4.1 illustrates the sensor and optical setup on the IHF. To allow for remote sensor control from the IHF control room, a ServSwitch CX Black Box was installed to communicate with the data acquisition system which was approximately 50 m away. This provided much improved communication between the sensor operator and the IHF test engineers. This also allowed for an opportunity to provide additional data to future IHF customers. Specifically, temperature and enthalpy profiles across the arc column. Once the data reduction process of the sensor is automated, test engineers will have immediate access to the LOS temperature and enthalpy data on their test run summaries. The automation process is currently ongoing and although it will require integration into the IHF data acquisition system, the current work has already resulted in an order of magnitude improvement in the time it takes to provide temperature and enthalpy results.

The data acquisition system manages the signal function generator and the laser controller. The laser is an external cavity diode laser (ECDL) and, for the data presented in the results section, is operated at a scan frequency of 500 Hz, resulting in a 1 kHz measurement rate due to the fact that the output frequency is scanned across the target transition twice in one sinusoidal cycle. The output of the ECDL is tuned in wavelength (1/ν) across the atomic oxygen transition centered near 777.19 nm (12,867 cm⁻¹). Here ν represents laser output frequency (cm⁻¹). A New Focus TLB-6900 Vortex II Series ECDL was used as the light source. Appendix A includes further details on the characteristics of the ECDL used and relevant information regarding operating procedures of this New Focus ECDL system. The laser head output power after single-mode fiber coupling is
approximately 15 mW. The fiber-coupled output of the laser is split into four single-mode fibers and pitched across the main gas stream through the four LOS in the optical disk. The light is coupled into four multi-mode fibers and routed to the detector box. The baseline laser intensity on each of the detectors within the detector box is approximately 2 mW.

Figure 4.1 The laser output is split into four equal-power beams and pitched across the arc column.

Research efforts prior to those included in this body of work improved the signal-to-noise ratio using a doublet lens catch optical system immediately upstream of each detector chip.[33] However, mechanical vibration-induced beam steering is still a significant source of noise. The optical access through-hole within the disk on each LOS is only 3 mm in diameter. This makes the optical system highly susceptible to beam steering and non-absorption intensity losses during the IHF runs. The beam steering-induced noise is additionally exacerbated by the high levels of blackbody emission.
generated by the high temperature gas. Although a bandpass filter centered at 780 +/- 10 nm is used, there is still a significant amount of emission detected. So much so that for high power cases, the amount of emission is multiple times greater than the detected laser intensity. The detector gain must be adjusted according to the IHF condition in order to avoid detector saturation during IHF runs. In light of these challenges, a considerable sensor optimization effort was undertaken to systematically reject the beam steering-coupled vibrational noise. This was accomplished by a thorough laser characterization effort.

A full characterization of the laser had not been completed prior to this study due to the extreme and incredibly difficult-to-recreate environment generated by the IHF. For example, the IHF’s maximum enthalpy condition requires approximately 6,000 A and 7,000 V. Typically when developing an absorption based sensor, the transition itself is used as a reference for characterizing the laser. The extreme IHF environment makes the task of characterizing the ECDL using the atomic oxygen absorbance feature as a reference a difficult one. Characterization of the laser involves understanding how the laser tuning range is affected by the scan frequency of the laser. The characterization effort is further complicated by the fact that the scan frequency affects the output frequency of the laser. This means that the output frequency of the laser is not known without a fixed-wavelength reference. Due to the sinusoidal nature of the output frequency of the laser, a wavemeter is also not well-suited to measure the output of the laser. The best reference in this case is the atomic oxygen transition itself. Due to the highly excited nature of this particular transition however, it is difficult to replicate
without the IHF running. IHF runs are limited in time and therefore do not allow for characterization during the minute long runs.

Instead, an alternative method was developed for creating a stable wavelength reference point. A mobile discharge cell was used to generate a narrow but detectable and visible transition. Although the chemical composition in this reference cell was not well characterized, it allowed for determination of the appropriate tuning parameters of the laser. It is important to point out that this discharge reference cell is not suited for determination of spectroscopic parameters as was the case with the reference cell used in the implementation of the biomass gasification sensor. A photo of the cell is shown in Figure 2.2. Figure 4.2 (a) contains a time domain plot of what the absorbance profile looks like for the breakdown of low-pressure air (< 0.1 Torr) in a reference cell. This allowed for a systematic understanding of the laser tuning range with respect to scan frequency. Figure 4.2 (b) contains these data. As the scan frequency increases, and thus the measurement rate increases, the range over which the laser can scan is reduced. Optimization of the laser tuning parameters through the use of the reference cell enabled the measurement rate to be increased from 100 Hz to 3.5 kHz. The “Optimized” data in Figure 4.2 (b) were collected by supplying the laser with its maximum amplitude input of 2.25 V. The sinusoidal input to the laser was also much higher than before. This allowed for a major reduction in the temporal resolution of the measurements being made, from 5.0 ms to 0.14 ms.
The increase in laser tuning range allowed collecting of data at pressures not previously measurable. Prior to this study, pressures beyond 6 atm could not be measured. Increased pressure results in increased collisional broadening of the absorbance profile. The previous maximum scan range of 1.8 cm$^{-1}$ as indicated by the Legacy data in Figure 4.2, is not sufficient to resolve the entire absorbance profile at these high-pressure conditions. The entire profile needs to be resolved in order to calculate the integrated area for use in Equation 2.1.

Sensor optimization resulted in a considerable expansion of the operational envelope of the sensor. From an operational standpoint, three parameters matter most when trying to assess the feasibility of making measurements for any given IHF run condition; current, add/main ratio, and pressure. Both current and add/main ratio provide a measure of how “hot” the gas stream will be at the measurement LOS. The pressure indicates how broad the absorbance feature will be. During previous operation of the laser, pressures greater than 6 atm were not measurable. The feature was too broad for a tuning range of only 1.8 cm$^{-1}$, however, a scan range of 3 cm$^{-1}$, which can now be

Figure 4.2 a) Absorbance profile of the reference cell and b) laser tuning range as a function of laser scan frequency.
achieved with the optimized system, is more than sufficient. As an example, the absorbance profile shown in Figure 2.3 requires a minimum of 2 cm$^{-1}$ for calculation of the integrated area.

Sensor optimization also allowed for measurements at increased add/main ratios. Increased add-air mass flow results in reduction of the LOS temperature measured at any given location downstream of injection and increases beam steering effects. The optimized sensor allowed for measurements at increased pressures and increased add/main ratios. Additionally, increased scan frequency of the laser resulted in suppression of some vibrational noise and allowed for an increase in signal-to-noise (SNR) ratio for most conditions. A method for quantifying the improvement in SNR is the temperature measurement uncertainty. Uncertainty for the temperature measurements is based on the residual fit to the absorbance profile. Integrated absorbance has a logarithmic effect on temperature as explained by Equation 2.1. Therefore, to calculate uncertainty, the percent residual is correlated to a change in temperature based on equilibrium calculations. On average, the temperature data reported in this study have an uncertainty of +/- 80 K. This is an order of magnitude improvement over measurements made using the un-optimized version of the sensor. This resulted in the ability to make measurements at lower temperatures. The minimum measurable temperature with this second-generation sensor is 5,150 K with a temperature uncertainty of +/- 300 K. This is compared to a temperature uncertainty in the first generation of the sensor of +/- 750 K for measurements near 5,000 K.
5. Biomass Gasifier: Multi-Species Sensing

5.1. Multi-Species Sensor Performance

The prototype multi-species sensor performance was validated in the laboratory by measurements in the gas cell of Figure 3.1. Measurements were conducted in pure gases as well as gas mixtures prepared with the mole fractions in Table 3.1 to mimic the expected gas composition producer gas made in the West Biofuels biomass gasifier. The uncertainties reported in Tables 5.1 and 5.2 are based on how well the absorption measurements matched known gas mixture compositions. Both wavelength-scanned DAS and WMS measurement schemes were evaluated in an atmospheric pressure and room temperature environment (296 K or 23 °C) with a path length of 1 m. For these sensor validation experiments the water vapor mole fraction was less than the 0.02 mole fraction of 100% relative humidity at room temperature. For safety reasons the CO gas mixture was limited to a mole fraction of 0.12. For in-the-field measurements at the West Biofuels facility, DAS and WMS mole fraction and measurement uncertainties were calculated based on fits to measured absorbance profiles using simulated Voigt line shapes and 2/1f simulations, respectively. Scanned WMS measurements were fit as per Goldenstein et al.[53] where the transition linecenter, integrated area, and collisional broadening are floated in the fitting algorithm. The mole fraction results and uncertainties are listed in Table 5.1 for DAS and Table 5.2 for WMS. Note that for the nearly noise free conditions in the laboratory the uncertainties for DAS and WMS are quite similar.
\[ x_i = \frac{P_i}{P_o} \]

### Table 5.1 Static cell measurements and uncertainty for 0.24 second averaging.

<table>
<thead>
<tr>
<th>Species</th>
<th>Gas Mixture Mole Fraction</th>
<th>DAS Laser Sensor Measured Mole Fraction (x_i)</th>
<th>Relative Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>0.0105</td>
<td>0.0097</td>
<td>7.6</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>0.0967</td>
<td>0.0938</td>
<td>3.0</td>
</tr>
<tr>
<td>CO</td>
<td>0.120</td>
<td>0.123</td>
<td>2.5</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0.200</td>
<td>0.202</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### Table 5.2 Static cell measurement uncertainty for WMS for 0.24 second averaging.

<table>
<thead>
<tr>
<th>Species</th>
<th>Gas Mixture Mole Fraction (x_i = \frac{P_i}{P_o})</th>
<th>WMS Laser Sensor Measured Mole Fraction (x_i)</th>
<th>Relative Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>0.0109</td>
<td>0.0114</td>
<td>5.5</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>0.102</td>
<td>0.114</td>
<td>12</td>
</tr>
<tr>
<td>CO</td>
<td>0.083</td>
<td>0.086</td>
<td>4.8</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0.200</td>
<td>0.204</td>
<td>2.0</td>
</tr>
</tbody>
</table>

It is important to note however that in the case for CH\(_4\), the uncertainties for DAS are lower than for WMS. The high absorbance of the CH\(_4\) transition led to high SNR and therefore reduced uncertainty. This indicates that in a reduced noise environment DAS can achieve performance as good as, and in this case better than,
WMS. In terms of laser selection, the noise environment should be carefully considered when designing a sensor and selecting a particular technique. Also worth noting is that when WMS background signals can be collected to correct for backgrounds, even lasers with large non-linear response can perform quite well.

5.2. Biomass Gasification Monitoring Field Test Results

The prototype sensor for the major species (H₂O, CH₄, CO₂, and CO) in producer gas was transported for measurements of almond pruning pellet gasification in the West Biofuels facility in Woodland, California. The sensor was attached to the reactor in the producer gas line of the gasifier before the tar reformer as illustrated in Figure 1.2 and shown in Figure 2.1. The four lasers were time-division-multiplexed and injection-current-modulated for proof-of-concept measurements using wavelength-scanned DAS and wavelength-scanned WMS as illustrated in the timing diagram in Figure 3.3. The transmitted intensity data for twelve scans was averaged and the mole fraction information extracted. Voigt fit data for wavelength-scanned DAS are illustrated in Figure 5.1, and the residuals indicate the goodness of fit. The fits in Figure 5.1 are representative for all measurements. Although the uncertainty varies slightly for each datum, this variability is quite small as evidenced by the minor error bars in Figure 5.2. The mole fraction values typical of these fits are those contained in Figure 5.2 below.
Figure 5.1 Wavelength-scanned DAS measurements (averaged over 0.24 seconds) with Voigt line shape fits taken in the West Biofuels gasifier; the difference between fit and measurement was used to determine measurement uncertainty. Typical mole fraction values for these fits are those contained in Figure 5.2.

The percent residual fits shown in Figure 5.1 are converted into an equivalent mole fraction. Representative uncertainty data are given as percent mole fraction in Table 5.3. As expected in the noisy environment of the field measurements, the scanned-WMS uncertainties are significantly smaller than those of scanned-DAS. The primary noise in the scanned-DAS measurements results from the attenuation of the transmitted intensity by particulate scattering and beam steering in the producer gas flow. The WMS measurement method is relatively immune from such effects.[16]
### Table 5.3

<table>
<thead>
<tr>
<th>Species</th>
<th>$U_{\text{DAS}}$ (%)</th>
<th>$U_{\text{WMS}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>1.0</td>
<td>0.13</td>
</tr>
<tr>
<td>CO</td>
<td>7.3</td>
<td>0.20</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.5</td>
<td>0.05</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.1</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Relative mole fraction percent uncertainties for scanned-DAS ($U_{\text{DAS}}$) and scanned-WMS ($U_{\text{WMS}}$) for 0.24 second averaging from fits to absorption line shapes acquired in field measurements in West Biofuel producer gas. Mole fraction values that correspond to these uncertainties are contained in Figure 5.2.

Time-resolved measurements of H$_2$O, CH$_4$, CO$_2$, and CO in the producer gas from the gasifier are shown in Figure 5.2 for wavelength-scanned-DAS and wavelength-scanned-WMS. These time-resolved laser-absorption measurements of producer gas have the time-resolution needed to optimize and stabilize the gasification process. Although the species mole fraction measured by the laser absorption sensor is relatively stable over the time monitored, variation in the mole fraction of important gasifier products CO and CH$_4$ suggest that process improvements are possible.

The laser absorption sensor is a research prototype and the gasifier is a research reactor, therefore sorting out what varies in time, the producer gas composition or the sensor performance, is a difficult matter. One solution to this problem would be to time-multiplex scanned-DAS and scanned-WMS lasers one right after the other. Since this would result in increased cost (number of lasers would double) and potentially limit the
number of species that could be measured, a different solution was found. The West Biofuels gasifier is equipped with two standard analytical chemistry instruments: gas chromatograph (GC) and a Fourier transform infrared (FTIR) spectrometer. Unfortunately, a direct comparison is not possible as the gas sampled for GC and FTIR must be filtered and dried, producing a significant time delay and diffusion in the gas conditioning equipment can smooth rapid time variation in gas composition. In addition, the GC measurements have multi-minute time response.

![Figure 5.2](image)

**Figure 5.2** Wavelength-scanned DAS (left panel) and wavelength-scanned WMS (right panel) measurements during biomass gasification.

Even with these drawbacks, it is quite useful to compare the laser absorption measurements with the GC and FTIR analysis. First, the laser absorption mole fractions must be converted from the wet basis of the *in situ* measurement to a dry basis since the FTIR and GC sample dried gas. The laser-measured water mole fraction is used to calculate the dry basis $x_{dry} = \frac{x_{wet}}{1-x_{H_2O}}$ for the other three species (CH$_4$, CO$_2$, and CO).
The dry-basis scanned-DAS and scanned-WMS laser absorption measurements of time-resolved mole fraction are compared with data from the GC and FTIR in Figure 5.3. There was a significant time difference between the scanned-DAS data and the scanned-WMS data; thus, if the gasifier stabilization was an issue, quantitative comparison of the DAS and WMS values is not meaningful.

Figure 5.3 Wavelength-scanned DAS (left panel) and scanned-WMS (right panel) laser absorption measurements (black) converted to dry basis mole fractions compared with GC (blue) and FTIR (red) data.
5.3 Biomass Gasification Field Test Discussion

The GC data are in excellent agreement with both DAS and WMS data, although during the DAS measurements there was only one GC data point and only two during the WMS data set. The FTIR has a two-minute measurement rate, so there are many more points to compare with the laser absorption sensor. Qualitatively, the time variations captured by FTIR data are in reasonable agreement with the laser-absorption sensor measurements and both diagnostics observe time variation in the composition of the producer gas. However, until the laser absorption sensor observed rapid time-varying gas composition, the gasifier operators had attributed the observed FTIR fluctuations to sensor and gas sampling problems. The observation of time varying producer gas composition by both laser absorption and FTIR led the operators to re-evaluate the gasifier operation, leading to the discovery of transients in the gasifier fuel feed system that produce unstable gasifier operation. Thus, the research testing of the laser absorption sensor enabled the West Biofuels team to improve the gasifier operation.

The laser absorption sensor provided the first direct measurements of H$_2$O at the West Biofuels biomass gasifier. Observation of much lower than expected H$_2$O mole fractions (4.5% instead of 7%) in the producer gas products also identified problems with the gasifier bed material. Thus, not only was the laser absorption sensor successfully demonstrated, but the initial research measurements of the sensor led to multiple improvements in the gasifier operation.
6. Arcjet Interaction Heating Facility: Enthalpy Sensing

6.1 Mixing Volume Characterization

With the optimized atomic oxygen sensor, the first goal was to replicate and confirm the results of Nations et al.[33] It is important to note here that the IHF operations are supported by various internal (NASA) and external customers. Measurement campaigns revolved around the characterization of the IHF MV. Measurements were made only under permission of the customers supporting IHF operations and when conditions allowed for absorbance measurements. There are many low temperature conditions where IHF can still operate but where there is not sufficient breakdown of oxygen to detect atomic oxygen absorption. Although input to IHF operators to specify specific run conditions was not allowed, measurements were made across multiple runs at repeated conditions over a range of add/main ratios. It is important to note this in order to explain the seemingly random nature of the run conditions for which measurements were made and that the conditions measured in previous studies,[32], [33] were not replicated exactly. However, test conditions at increased pressures and greater add/main flow ratios over various levels of the IHF operating current were measured. In the cases where conditions match those of previous studies, results compare well.

The data in Figures 6.1 and 6.2 represent LOS measurements made at Disk 4 for various conditions. These data confirm prior observations of a uniform temperature profile. Theoretical temperature profiles for these conditions result in a top hat profile with a sharp drop in temperature near the walls. Figure 6.3 highlights this effect. At these
conditions the temperature profile is nearly flat, which is what the data at Disk 4 confirm. Figure 6.1 also illustrates how repeatable the conditions in IHF are. The 3.7 atm condition in Figure 6.1 was measured multiple times. Only two separate measurements are shown here for clarity. The data for this condition are consistently near 6,500 K. These data provide evidence of the repeatability of the facility as well as the sensor. The 2 atm case in Figure 6.1 is considered the lower limit for this sensor. The low facility current and non-minimal add/air ratio result in minimal absorbance and thus SNR. This is also why the uncertainty is greater for this case. This low peak absorbance ($\alpha \approx 0.10$) case results in a lower SNR. The reduced absorbance is due to both the low pressure and low temperature of the gas. Low pressure results in a lower number density of oxygen available for breakdown. The reduced temperature results in a less populated lower state number density of atomic oxygen for the transition under investigation. The SNR and thus measurement uncertainty for this sensor is therefore inherently linked to the measured absorbance.

Figure 6.1 Mid to low current conditions at Disk 4. The 2 atm condition is the lower temperature limit for the sensor. The data in black represent three separate runs at the same conditions.
Figure 6.2 Maximum current conditions at Disk 4. Relatively flat temperature profiles indicate uniform flow.

A comparison of Figures 6.1 and 6.2 reveals an interesting near-wall effect that varies as a function of the three primary parameters of interest: add/main fraction, MV pressure, and arc-heater current. For Figure 6.1, the data at the LOS closest to the wall, \( \frac{r}{r_0} = 0.85 \), is absent. This is due to the observed lack of absorbance near the wall. There are multiple effects at work here. Firstly, the heat loss to the walls due to the internal water cooling of the copper disks that make up the enclosure for the column of arc-heated gas creates the sharp drop in temperature which results in a reduced breakdown of molecular oxygen and thus a reduced number density of our target species, atomic oxygen. A second temperature reduction effect results from an increased boundary layer at reduced temperatures for this type of confined flow. With this LOS being so close to the wall, the beam path is within the boundary layer and reduces the LOS absorbance entirely. A third effect responsible for the reduced level of atomic oxygen is a film cooling effect caused by the add-air injection process. For some conditions, the fluid dynamic effects caused by add-air injection might force the injected air to remain close to
the wall even, L/D = 2.1. Investigation of the fluid dynamic effects caused by the add-air injection is the focus of a future and currently ongoing study. The complete work reported here is helping to design these future studies.

![Figure 6.3 CFD computation of temperature profile across the MV in the IHF. Temperature drops steeply near the wall.](image)

The fact that the measurements at Disk 4 indicate a flat temperature profile not only confirms previous studies but more importantly provides strong evidence for a homogeneous core and therefore well-mixed gas stream. The add-air injected upstream has mixed sufficiently well with the main flow and thus provides a uniform stagnation pressure and heat-flux profile at the nozzle exit. An annulus with a thickness of 10%-15% of the radius, likely depending on test conditions, still makes up the boundary layer and/or the add/main mixing layer. This confirms that installation of the MV has satisfied the goal of improving flow uniformity at the nozzle inlet. The next set of measurements were focused on confirming an axial location along the MV where the injected add-air
had not fully mixed with the core flow. Measurements were made at Disk 1 not only to confirm previous studies but also to expand on the dataset of unmixed temperature profiles in the IHF. Prior to this study only four measurements at a similar, unmixed region, had been recorded. The importance here was to gain a better understanding of what the temperature profile of the flow was prior to the addition of the MV.

The data in Figures 6.4-6.6 are all measurements made at Disk 1. Disk 1 is adjacent to and immediately downstream of add-air injection, the length-to-diameter ratio between injection and the Disk 1 LOS is L/D = 0.07. In the lower to mid power cases like those in Figure 6.4, the injected add-air has a more significant effect on the overall temperature profile. Although the option to make measurements at exactly the same run conditions at both disks was not available, one condition was repeated for Disk 4 and Disk 1. The 5.6 atm condition in Figure 6.4 is the same condition shown in Figure 6.1. The mean temperatures for Disk 1 and Disk 4 are 6,769 K and 5,219 K, respectively, a 23% drop in temperature from Disk 1 to Disk 4. This suggests a correlation between the installation of the MV and the resulting 20% decrease in observed heat flux measurement by IHF customers.
Figure 6.4 Low to mid power (current) conditions at Disk 1. Add-air near the wall and low amperage conditions provide insufficient breakdown of oxygen at LOS D.

The temperature profiles at Disk 1 are consistently more parabolic. This add-air effect can be seen more pronounced for conditions with add/main flow ratios greater than unity. Figure 6.5 contains data for high-power conditions, with arc-heater currents ≥ 4,000 A. The 4.1 atm case with an add/main ratio = 1.7, further illustrates the asymmetric and parabolic temperature profile at Disk 1. This high add-air case also showcases the sensor’s ability to effectively make measurements under high add-air conditions, a type of measurement that previously could not have been made. This increased sensing capability is attributed to the suppressed mechanical vibration noise. The increased laser scan rate and the window fouling mitigation helped reduce beam steering effects and increased SNR. Another instance of the high-add air effects can be seen in Figure 6.6. Both of the higher pressure cases in Figure 6.6 were run under minimal add-air conditions. This is routinely done when add-air is not a desired test parameter but rather required by the facility to prevent add-air line damage (melting). For two of these cases, all four LOS were sufficiently hot to allow for a temperature measurement. The 3.9 atm
case however had sufficiently high add-air to prevent a measurable amount of absorbance. These data are helpful in understanding the levels of add-air that require additional axial distance for sufficient mixing.

**Figure 6.5** High energy conditions at Disk 1. High add-air case shows significant asymmetry. Although higher in amperage than the lower power cases, it is still not sufficient to see atomic oxygen at LOS D.

**Figure 6.6** Maximum power cases. High add-air condition at Disk 1 shows unstable temperature profile.
The measurements at Disk 1 and 4 allowed for increased understanding of the boundaries of homogeneous temperature profiles along the MV. The data confirm the temperature profile instabilities at Disk 1 and the homogeneous and flat temperature profiles at Disk 4 for various IHF conditions. By the time the flow has had approximately two main-flow diameters of evolution along the MV, the injected add-air has mixed sufficiently with the main flow and any resulting drop in temperature is likely due to the cooling of the arcjet column. Next, measurements were made to better document how temperature at the centerline of the disks evolved axially along the MV. For reference, IHF instrumentation have shown that for spacer disks in the cathode (cathode is downstream of anode) there is approximately a heat loss of 800 W/cm² per disk. This varies with IHF conditions. Although difficult to compare to temperature drop along the MV, it provides some quantitative measure of the heat loss due to the disks.

Figure 6.7 contains data for three separate runs. Unfortunately for one run, the centerline LOS at Disk 4 was obstructed by an accumulation of copper soot that originated from erosion of the copper electrode packages upstream of the MV. It is now standard practice to clean the windows with every nozzle or electrode package change which occurs after 3-5 hours of arc-heater run time. The 1.8 and 3.5 atm cases were measured after the window fouling was identified. The effect of add-air injection on the centerline temperature is well illustrated by these three cases. The condition with the highest amount of add-air undergoes a 585 K change in temperature from Disk 1 to Disk 2. At Disk 1, add-air injection has a minimal effect, if any, on the centerline temperature. Add-air injection is intended to reduce the overall enthalpy of the flow. What is not so obvious however, is the extent of mixing that occurs as a function of axial distance along
the MV. These centerline data indicate that the majority of the mixing is occurring somewhere between Disk 1 and Disk 2, the details of which are described below. This is a significant finding because Disk 1 is located precisely where the optical disk was located prior to the MV installation, which was immediately upstream of the nozzle inlet. This highlights the improvements in mixing that the MV facilitates. The MV was installed to eliminate the asymmetry that was observed for high-add air conditions but had the negative effect of reduced enthalpy capability. With the MV installed, how mixing evolves for various add-air conditions could be explored.

![Figure 6.7](image)

**Figure 6.7** Centerline LOS measurements. High add-air cases show significant temperature drop.

The data between Disks 2 and 3 suggest that mixing has already occurred or is near completion due to the very similar drop in temperature for all three conditions. The drop in temperature between Disks 2 and 3 is, $\Delta T_{2-3} = 221$ (3%), 296 (4%), and 242 K (3%) for the 1.8, 3.5, and 5.4 atm conditions, respectively. Those are relatively similar levels of temperature drop for widely varying levels of add-air, 200%-300% difference.
This confirms the measurements made by Nations et al.[32] where even minimal add-air conditions resulted in asymmetric temperature profiles at Disk 1. The temperature drop seen after Disk 1 is a strong function of injected add-air.

Another indicator for mixed flow is the less significant drop in temperature between Disks 3 and 4, \( \Delta T_{3.4} = 136 \) and 105 K for the 1.8 and 3.5 atm conditions, respectively. This suggests that there is a minimal amount of mixing occurring between Disks 3 and 4 and that it is relatively independent of the amount of add air used. A combination of centerline and disk LOS data can be used to generate a functional relationship between the axial distance needed for uniform flow versus the amount of injected add-air. For example, the lowest add-air case, add/main = 0.10, appears to have achieved sufficient mixing before or very near Disk 2. For the higher add-air case however, add/main = 0.33, the mixed axial distance is likely somewhere in between Disks 2 and 3. Although these observations are only qualitative, a reorganization of the optical disks could quantitatively verify the location of adequate mixing for each run condition. In doing so, the facility could shorten the MV and recapture some of the lost enthalpy.

As a check to the consistency of the IHF over time, time resolved measurements were made for one specific run. The run conditions for this particular run are; \( P = 7.7 \) atm, add/main = 0.07. Figure 6.8 contains time resolved data over a single run. As a temperature profile, the mean temperature data in Figure 6.8 is asymmetric with LOS A having a difference of approximately 600 K. At this point in time in the experimental development and implementation of the sensor, blackbody emission in the MV was not properly mitigated for. Shortly after these data were collected, the emission problem was
resolved. The 7.7 atm data shown in Figure 6.1 points out that this case does in fact have a flat temperature profile. Figure 6.8 is included here to illustrate the steadiness of the MV conditions and the ability of the sensor to capture transient behavior.

**Figure 6.8** Time resolved temperature measurements during a single run in the IHF. The arc-off shutdown transient is evidenced by the sharp drop in temperature.
6.2. Enthalpy Sensing

Assuming thermochemical equilibrium at each LOS provides knowledge of the chemical composition of the gas. The thermochemical equilibrium assumption is discussed in more detail in Appendix B. The flow rates of main flow, add-air, and the small amount of argon used to shield the cathodes and promote arc attachment are measured and known. Combined with the facility measured pressure in the MV, the centerline enthalpies are calculated. The enthalpy data in Figure 6.9 is the result of calculating enthalpy based on the temperature data shown in Figure 6.7. The temperature error bars were converted to an enthalpy value and reported as error bars in Figure 6.9.

![Figure 6.9](image.png)

**Figure 6.9** Centerline enthalpies based on the temperature data shown in Figure 6.7. Amount of add-air significantly impacts the cooling at Disks 1 and 2. Sonic throat and energy balance enthalpy measurements are included as well. The black dashed line indicates the approximate location of the nozzle entrance.
On average, the uncertainties shown in Figure 6.9 are +/- 0.9 MJ/kg. These data help to point out how significant an effect the MV installation has had on the centerline enthalpies and overall bulk enthalpies. For example, prior to installation of the MV, Park et al. [28] report a sonic throat enthalpy of 28.8 MJ/kg (add/main ~ 0.1, P = 4.5 atm, I = 6,000 A). For a similar condition (add/main = 0.2, P = 3.5 atm, I = 6,000 A), a mean centerline enthalpy of 20 MJ/kg was calculated. Although a direct comparison cannot be made, this helps to contextualize the enthalpy losses due to installation of the MV.

It is possible however, to make a comparison with current methods used by the IHF facility to measure bulk enthalpy in the facility. These are indicated by the red and blue dashed lines in Figure 6.9. Nominally, any IHF run will have two types of enthalpy values calculated. The first is a sonic flow calculation[28] and the second is a differential energy balance method.[59] For the 2,500 A case shown in Figure 6.9, the sonic throat and energy balance enthalpies are 12.2 MJ/kg and 16.6 MJ/kg, respectively. For the 3,500 A case, the two enthalpies are 16.4 MJ/kg and 17.4 MJ/kg, respectively. It’s important to note that the energy balance measurements reported here should be used with discretion, as these numbers have been known to vary somewhat historically.

These data and comparisons provide a great opportunity to better understand the mixing behavior and potentially reduce the MV length. It also provides the IHF with a non-intrusive, quantitative, and spatial measure of the facility’s bulk and centerline enthalpy. This is highly valuable to those involved with IHF operations, IHF customers, and computational fluid dynamics modelers. There exist very few non-intrusive and quantitative measurement techniques. Grinstead et al. have demonstrated the use of laser induced fluorescence (LIF) in arcjet environments.[60], [61] LIF provides spatial number
density and temperature measurement as well, however it is limited to single-point measurements. The LOS path average feature of scanned-DAS allows for a quantitative evaluation of the mixing behavior with many less measurements. These non-intrusive diagnostic methods, in combination with computational solutions, are well-suited to provide increased understanding of the arcjet environment in support of greater space transportation endeavors.

This study has not only validated the ability to locate the axial distance at which the flow’s temperature profile becomes relatively flat and homogeneous in terms of mixedness, it also provides an opportunity to study different methods of add-air injection. It is clear from the data in Figure 6.9 that there is an opportunity to recapture some of the enthalpy losses simply by decreasing the length of the MV. In addition, by leveraging decades of jet-in-cross-flow research, the sensor can be used to study the fluid dynamic interaction in the IHF and provide additional recapturing of enthalpy losses by leading to a more efficient add-air mixing scheme. This work is the subject of a study currently underway.
7. Conclusions

7.1 Biomass Gasification Sensing

A multi-species sensor was designed for time-resolved monitoring of the major species (H\textsubscript{2}O, CH\textsubscript{4}, CO\textsubscript{2}, and CO) in the producer gas output of a pilot-scale biomass gasifier operating on pellets made from almond pruning. The producer gas output was not stable during the sensor test campaigns, making it difficult to determine if the time-variation in the observed species concentration was due to the gasifier or the sensor performance. Thus, the laser absorption sensor performance reported in Table 5.3 was based on residuals between the measured absorbance data and the line shape fits used to extract mole fraction. However, the absorption sensor monitored the gas composition with the time resolution needed for gasifier control. In addition, the sensor identified two problems with the gasifier operation: first, the low H\textsubscript{2}O content observed in the producer gas demonstrated that the bed material required replacement/regeneration, and second, the observed rapid time-varying gas composition was traced to problems with the fuel feeding of the fuel pellets.

With regard to the comparison of the scanned-DAS and scanned-WMS techniques, scanned-WMS performed better than scanned-DAS. This is evidenced by the relative uncertainty data in Table 5.3. Whether DAS or WMS should be implemented, largely depends on the performance requirements of the application under consideration. It should also be noted that scanned-WMS, albeit complex to implement, is considered better suited for real-time monitoring of a system.
Guidelines for laser device selection for WMS sensors were described and the need for linear response of the diode laser wavelength to injection current variation was identified. A method for mitigating the adverse effects of a varying WMS background was also provided.
7.2 Arcjet Mixing Volume Characterization

Motivated by a need to understand add-air mixing behavior, scanned-DAS absorption spectroscopy was implemented in the MV of the IHF. Although a scanned-DAS sensor had been used to study mixing in the IHF MV prior to this study, the sensor was not capable of measuring the full range of the IHF conditions. Specifically, high add-air and high pressure conditions were beyond the previous sensor’s capabilities. This study’s first focus was to optimize the sensor and expand the sensing capabilities to better understand high-add air and high pressure conditions. A discharge cell was created as a stable wavelength reference that allowed for a thorough characterization of the laser (ECDL). Wavelength tuning range was improved and enabled measurements at high add-air and high pressure conditions.

Next the study focused on understanding temperature profiles at non-uniform and uniform locations along the MV. The improved sensor was able to confirm uniform flow and flat temperature profiles at Disk 4, immediately upstream of the nozzle inlet. Measurements made at Disk 1 confirmed non-uniform conditions for high-add air cases. Conditions with relatively high add-air were quantified using the optimized version of the sensor. These are conditions that were previously undetectable. Measurements also showed consistent repeatability of the IHF test conditions. Disk 1 temperature profiles were also found to be significantly more parabolic in shape that was attributed to the effects of add-air injection.

Centerline measurements showed a strong relationship between injected add-air and the axial distance required for sufficient mixing. A similar slope in temperature loss for all
three cases measured indicates a significant opportunity for recapture of lost enthalpy capability for the IHF. A combination of disk and centerline measurements can help locate the minimum MV axial distance needed for uniform flow. This sensor now provides an opportunity to implement potentially more efficient add-air mixing techniques to achieve mixing more rapidly and reduce the size of the MV, thus recapturing some of the IHF’s enthalpy losses.
8. Future Work

8.1 Biomass Gasification Sensing

The sensor development and implementation efforts reported in this body of work validated the sensing requirements for WestBiofuels. This sensor was a prototype meant to validate the sensing strategy. Future efforts will focus on installing an \textit{in situ} sensor immediately downstream of the producer gas output of the gasifier instead of 50 ft downstream.

Another chemical species of interest to WestBiofuels is H$_2$S. There were efforts in the early modeling of the multi-species sensor that identified a transition in the near-infrared that would be suitable for measuring H$_2$S mole fraction. Unfortunately, this would have required a new diode laser. Due to a lack of resources, it was not implemented in this initial prototype sensor. A future iteration of the prototype multi-species sensor developed in this body of work, however, could be incorporated and implemented.

Finally, there is a potential to incorporate single-ended sensing in this system. The pathlength and optical access immediately upstream of the producer gas outlet is shorter than 1 m and the facility is not entirely amenable to multiple optical access windows. A single-ended sensor would be a suitable solution for both the limited pathlength and make it easier to integrate into the WestBiofuels facility.
8.2 Arcjet Enthalpy Recapture

Despite optimization of the sensor and increased sensing capabilities, beam steering is still a considerable source of noise. This extreme environment is an ideal candidate for scanned-wavelength modulation spectroscopy (WMS). Scanned-WMS is an excellent diagnostic method for eliminating beam steering interference and mitigating black body emission interference. However, the implementation is quite involved and should be avoided if scanned-DAS can be implemented instead, as was done in this study. Although scanned-DAS was successfully implemented, due to the specific laser source that was used in this study (ECDL), the data reduction process is time consuming and therefore does not lend itself well to real-time sensing of temperature and enthalpy. Unlike linearly responsive laser diodes that are typically used for gas sensing applications, ECDL systems do not respond linearly to forward current. This non-linear baseline and the disturbance caused by the beam steering makes the task of calculating a non-absorbing baseline time consuming and does not lend itself to automation. Automation in the IHF would be valuable since it could provide a real-time and quantitative measure of the bulk or centerline enthalpy of the facility.

Implementation of scanned-WMS would resolve these issues and reduce measurement uncertainty, although, a new light source would be needed. The ECDL used in this study is limited to a scan frequency of 3.5 kHz. Scanned-WMS requires modulation rates of at least 10 kHz. There is also the issue of laser power output. Since the fiber coupled output is split into four separate beams, after coupling losses, the resulting power on the detector is approximately 2 mW. A relatively high power and high frequency modulation capable laser would be needed to implement scanned-WMS.
successfully. One way to help with the output power issue is to optimize the coupling and pitching of the laser across the MV. The current setup experiences about a 30% power loss across the MV.

In terms of application of the sensor, there is still an opportunity to provide further insight into the add-air mixing behavior of the IHF. Figure 8.1 is a diagram of a single add-air disk and a photo of the assembly of add-air disks showing the inner surface of the disks that make up the MV. The add-air interacts with the flow in an azimuthal manner. Sheets of high velocity (sonic) room temperature air penetrate the main flow. Figure 8.1 helps to illustrate just how close to the optical disk add-air injection takes place. As a reminder, prior to the MV installation, the inlet to the nozzle was immediately downstream of the optical disk, only 0.7 main-flow diameters away. In the current setup, the disk immediately downstream of Disk 1 is the axial location most representative of the location of the nozzle inlet prior to MV installation. It is intuitive now that for high add-air conditions, there would be a significant amount of non-uniform flow.

![Add-air disk flow path](image)

**Figure 8.1** Photo of the interior of the arc column. Three LOS are indicated by the red dots on Disk 1. Flow here is right to left.
A. Atomic Oxygen Sensor Details and Guidelines

A.1 ECDL Non-Linearity

One of the major differences in the sensing strategies between the biomass gasification and atomic oxygen sensors is the light source used. In each case, the tuning of the lasers is accomplished differently. The DFB lasers in the biomass gasification sensor are tuned via injection current. Notwithstanding the minor non-linear effects at high frequency operation, DFB diodes behave linearly to injection current. This means that the tuning of the laser will respond sinusoidally for example, when a sinusoidal signal is generated by the system. This key feature of DFBs makes calculation of the baseline intensity of the transmitted laser signal a relatively easy and automation friendly task.

However, DFBs have a power limitation. For example, the CyOptics and NTT diodes used in the biomass gasification sensor had 5 mW and 10 mW of output power, respectively. In the case of the IHF sensor, this amount of power would simply not suffice. The sensor would have to be made up of four separate diode lasers (costly) or the output power, since there are four LOS, would be split into four and after coupling losses would be insufficient to provide a readable signal on the detectors.

For the above mentioned reasons, other options for a light source were explored for sensing in the IHF. The New Focus ECDL provided sufficient power for four LOS at a laser head output power of approximately 20 mW. After fiber and free space coupling, each detector sees approximately 2 mW of power. While this source provided sufficient power, the non-linear response to the DAQ generated signal results in an unusual baseline
intensity. Figure A1 contains baseline intensity as well as transmission intensity during an IHF run at Disk 4. The conditions for this IHF run are as follows, $P = 1 \text{ atm}$, add/main $= 0.6$, and a mean profile temperature of 6,200 K. The signal generated by the DAQ in this case is sinusoidal at a frequency of 500 Hz. The target transition (777.2 nm) therefore is scanned in wavelength space twice within the 2 ms sinusoidal cycle. The location of the peaks in the time domain is evidenced by the acute reduction in intensity, indicated by the dotted lines.

**Figure A.1** Baseline ($I_o$) intensity in red, and ($I$) and transmission intensity during an IHF run. Baseline intensity is recorded while arc heater is off.

The shape of the baseline intensity in Figure A.1 is problematic since it makes calculating the baseline intensity by using a linear or sinusoidal fit, as is the case with DFB based diode sensors, a much harder task. The fact that the baseline is non-linear, makes the data reduction and calculation of a baseline much more time consuming. The
method for calculating the baseline also becomes dependent on the set IHF condition. This creates increased uncertainty in the calculated temperature.

For example, the data contained in Figure A.1 has a low peak absorbance, $\alpha \sim 0.10$. Figure A.1 shows that the intensity variations in the laser response have an amplitude of nearly half of the amplitude of the peak absorption features. This is relevant to the fitting algorithm that is implemented to calculate the integrated area of the absorption feature. When the absorbance is low, as is the case in the Figure A.1 data, the location of the baseline significantly impacts the total calculated integrated area. This is because the area under the wings of the transition, is a considerable fraction of full-width half-maximum area under the curve. The increased uncertainty is evidenced by the increase in the size of the error bars in the IHF data presented in previous sections.

High absorbance (i.e. high temperature and pressure conditions) clearly have a reduced uncertainty, as indicated by the reduced error bars in the IHF data presented above. In the high absorbance cases, the non-linear intensity fluctuations are negligible compared to the high peak absorbance features, $0.4 \leq \alpha \leq 2$. At approximately $\alpha = 0.4$, the uncertainty improves and the fitting process is much more straightforward.
A.2 ECDL Use Guidelines

The non-linearity in signal response mentioned in the previous section is due to the design of the ECDL. Whereas DFBs are electronically tunable [62], an ECDL requires mechanical tuning. Figure A.2 diagrams the components of an ECDL.[63] The mechanical tuning in the this system is accomplished by a piezo-electric motor that rotates along the pivot point and displaces the retroreflector to achieve a change in the wavelength/frequency output of the laser system. This is the limiting factor in the operational scan frequency that the signal generator should be set to. The piezo-electric motor can be set to DC-3.5 kHz modulation (i.e. scan frequency).

![Diagram](image)

**Figure A.2** Major components in the New Focus TLB-6900 ECDL. The ECDL implements a Littman-Metcalf laser cavity system.

Another critically important control parameter for the laser is the amplitude of the generated signal that is sent to the laser controller. New Focus recommends signal values within ± 4.5 V and to not exceed a peak-to-peak value of $V_{p-p} = 4.5$ V. To be clear, these
are the Frequency Modulation inputs on the back of the laser controller. New Focus gives guidelines for the maximum voltage of the externally generated DAQ signal. Voltages above 100 V will result in operating in a non-mode hop free zone. The maximum recommended voltage, DC level (set on laser controller) plus Frequency Modulation input is 117.5 V. CAUTION, operation of the system at 117.5 V led to damage of the piezo-electric motor and months worth of lead time. Operation of the system at greater than 100 V is highly discouraged.
B. Thermo-Chemical Equilibrium Assumptions

The basis for the LTE assumption rests primarily on the high-pressure environment contained within the IHF MV. As a reminder the MV is downstream of the arc heater. The MV of the IHF also experiences pressures that range between 1-9 atm in the MV. Pope has shown, that for arc heater reservoir pressures of 0.2-0.37 atm, the flow was found to be near equilibrium at the nozzle entrance and remained chemically frozen until it reached the nozzle exit.[34]

Park[64] and Nations[65] also discuss the basis for the LTE equilibrium assumptions used in the analysis of experimental results in the IHF. In short, there are two factors to consider in assuming thermodynamic equilibrium: chemical equilibrium and Boltzmann statistics. As the temperature and pressure of a gas is increased to levels obtained in the IHF, the likelihood that a collision will result in a reaction increases, thus increasing the rate at which chemical equilibrium is reached. Additionally, at IHF MV pressures, the rate of collisional excitation and de-excitation are high compared to the energy depleting rates of radiative emission. Thus, the population of the various energy levels of the gas particles can be described by Boltzmann statistics.

As Laux et al.[66] point out, there are cases when atmospheric plasmas exhibit nonequilibrium behavior. This occurs when the convective rates of a plasma are faster (~1 km/s) than the rates of chemical reaction. In the IHF MV, convective rates are much lower (~100 m/s). Although some air arcjet plasmas may exhibit nonequilibrium behavior, by the time the flow reaches the high pressures expected in the MV, it has proven sufficient to assume LTE at the measurement locations within the MV.
A sure method for verifying LTE would be to measure transitions of different energy modes. In the IHF this is somewhat difficult to accomplish since air is the working fluid. However, the arcjet complex at ARC has recently reactivated a smaller 10 MW arcjet facility. This facility has the capability to study more than just air conditions. Gas mixtures with species like CO$_2$ could be used to more readily access near-IR bands and compare electronic, rotational, and vibrational bands. This would provide more definitive evidence about the thermal-chemical equilibrium assumptions made of the gas. It could also shed light on how far away from the arc these assumptions become valid.
References


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