I dedicate this work to my parents
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The widening gap between the demand and supply of fossil fuels has catalyzed the exploration of alternative sources of energy. Interest in the power, water extraction and refrigeration (PoWER) cycle, proposed by the University of Florida, as well as the desirability of using biofuels in distributed generation systems, has motivated the exploration of biofuel vitiated combustion. The PoWER cycle is a novel engine cycle concept that utilizes vitiation of the air stream with externally-cooled recirculated exhaust gases at an intermediate pressure in a semi-closed cycle (SCC) loop, lowering the overall temperature of combustion. It has several advantages including fuel flexibility, reduced air flow, lower flame temperature, compactness, high efficiency at full and part load, and low emissions. Since the core engine air stream is vitiated with the externally cooled exhaust gas recirculation (EGR) stream, there is an inherent reduction in the combustion stability for a PoWER engine. The effect of EGR flow and temperature on combustion blowout stability and emissions during vitiated biofuel combustion has been characterized. The vitiated combustion performance of biofuels methyl butanoate, dimethyl ether, and ethanol have been compared with n-heptane, and varying compositions of syngas with methane fuel. In addition, at high levels of EGR a sharp reduction in the flame luminosity has been observed in our experimental tests, indicating the onset of flameless combustion. This drop in luminosity may be a result of inhibition of processes leading to the formation of radiative soot particles. One of the objectives of this study is finding the effect of EGR
on soot formation, with the ultimate objective of being able to predict the boundaries of flameless combustion. Detailed chemical kinetic simulations were performed using a constant-pressure continuously stirred tank reactor (CSTR) network model developed using the Cantera combustion code, implemented in C++. Results have been presented showing comparative trends in pollutant emissions generation, flame blowout stability, and combustion efficiency.
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<td>Symbol</td>
<td>Description</td>
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<tr>
<td>--------</td>
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</tr>
<tr>
<td>$S$</td>
<td>Species concentration vector, mol/m$^3$</td>
</tr>
<tr>
<td>$s$</td>
<td>Soot surface area, cm$^2$/m$^3$</td>
</tr>
<tr>
<td>$SN$</td>
<td>Smoke number</td>
</tr>
<tr>
<td>$\dot{s}_j$</td>
<td>Species surface production rate, mole/s·m$^2$</td>
</tr>
<tr>
<td>$t_0$</td>
<td>Igniter gaussian-pulse peaking time, s</td>
</tr>
<tr>
<td>$U$</td>
<td>Internal energy, J</td>
</tr>
<tr>
<td>$V_R$</td>
<td>Reactor Volume, m$^3$</td>
</tr>
<tr>
<td>$W_r$</td>
<td>Moment production rate due to surface chemistry, mol/ m$^3$·s</td>
</tr>
<tr>
<td>$Y_{j,s}$</td>
<td>Mass fraction of species $S_j$ in stream $s$</td>
</tr>
</tbody>
</table>

| Greek  | |
|--------||
| $\alpha$ | Air-fuel Ratio |
| $\alpha_{st}$ | Stoichiometric air-fuel Ratio |
| $\beta_{i,j}$ | Collision frequency for coagulation |
| $\epsilon$ | Van-der waal’s collision enhancement factor |
| $\eta_c$ | Combustion efficiency (combined conversion efficiency) |
| $\phi$ | Equivalence ratio |
| $\mu_r$ | $r^{th}$ size moment, mol/ m$^3$ |
| $\sigma_I$ | Igniter gaussian-pulse width (given as full-width-half-maximum), s |
| $\tau_{res}$ | Residence time, s |
| $\dot{\omega}_j$ | Species production rate, mole/s·m$^3$ |

| Subscripts | |
|------------||
| $A$ | Air |
| $F$ | Fuel |
| $R$ | EGR |
| $j$ | Species index |

| Superscripts | |
|--------------||
| $c$ | Continuum coagulation regime for soot formation |
| $f$ | Free-molecular coagulation regime for soot formation |
| $t$ | Transition coagulation regime for soot formation |
| $sc$ | Surface condensation of PAH on soot particules |

<p>| Abbreviations | |
|---------------||
| ASU | Air separation unit |
| BO | Blowout |
| CI | Compression ignition |
| CFD | Computational fluid dynamics |
| CGC | Cool gas cooler |</p>
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CNG</td>
<td>Compressed Natural Gas</td>
</tr>
<tr>
<td>CCGT</td>
<td>Combined cycle gas turbine</td>
</tr>
<tr>
<td>CSTR</td>
<td>Continuously stirred tank reactor</td>
</tr>
<tr>
<td>CRGT</td>
<td>Chemically reformed gas turbine</td>
</tr>
<tr>
<td>COSTAIR</td>
<td>Continuous staged air combustion</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential Mobility Analyzer</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethyl Ether</td>
</tr>
<tr>
<td>EI</td>
<td>Emission Index</td>
</tr>
<tr>
<td>EGR</td>
<td>Exhaust gas recirculation</td>
</tr>
<tr>
<td>EGRT</td>
<td>Exhaust gas recirculation temperature</td>
</tr>
<tr>
<td>ExV</td>
<td>Exhaust valve</td>
</tr>
<tr>
<td>EPFM</td>
<td>Eulerian particle flamelet model</td>
</tr>
<tr>
<td>FLOX</td>
<td>Flameless oxidation</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-width-half maximum</td>
</tr>
<tr>
<td>HGC</td>
<td>Hot gas cooler</td>
</tr>
<tr>
<td>HiRC</td>
<td>High Recirculation Combustion</td>
</tr>
<tr>
<td>HPC</td>
<td>High-pressure compressor</td>
</tr>
<tr>
<td>HPT</td>
<td>High-pressure turbine</td>
</tr>
<tr>
<td>HTC</td>
<td>High temperature combustion</td>
</tr>
<tr>
<td>HACA</td>
<td>Hydrogen-abstraction-acetylene-addition</td>
</tr>
<tr>
<td>HCDI</td>
<td>Homogenous Charge Diffusion Ignition</td>
</tr>
<tr>
<td>HiTAC/HTAC</td>
<td>High temperature air combustion</td>
</tr>
<tr>
<td>HPAC</td>
<td>Highly preheated air combustion</td>
</tr>
<tr>
<td>HPRTE</td>
<td>High pressure regenerative turbine engine</td>
</tr>
<tr>
<td>HRSG</td>
<td>Heat recovery steam generator</td>
</tr>
<tr>
<td>IC</td>
<td>Internal combustion</td>
</tr>
<tr>
<td>JSR</td>
<td>Jet-stirred reactor</td>
</tr>
<tr>
<td>IGCC</td>
<td>Integrated gasification combined cycle</td>
</tr>
<tr>
<td>LP</td>
<td>Loading parameter</td>
</tr>
<tr>
<td>LDV</td>
<td>Laser doppler velocimetry</td>
</tr>
<tr>
<td>LNI</td>
<td>Low NOx Injection</td>
</tr>
<tr>
<td>LPC</td>
<td>Low-pressure compressor</td>
</tr>
<tr>
<td>LPT</td>
<td>Low-pressure turbine</td>
</tr>
<tr>
<td>LTC</td>
<td>Low temperature combustion</td>
</tr>
<tr>
<td>LLNL</td>
<td>Lawrence Livermore National Laboratory</td>
</tr>
<tr>
<td>LTHR</td>
<td>Low temperature heat release</td>
</tr>
<tr>
<td>MK</td>
<td>modulated kinetics</td>
</tr>
<tr>
<td>MAI</td>
<td>Main air inlet</td>
</tr>
<tr>
<td>MB</td>
<td>Methyl Butanoate</td>
</tr>
<tr>
<td>MFR</td>
<td>Mass flow regulators</td>
</tr>
<tr>
<td>MILD</td>
<td>Moderate and intensive low oxygen diluted</td>
</tr>
<tr>
<td>NAAQS</td>
<td>US national ambient air quality standard</td>
</tr>
<tr>
<td>NOC</td>
<td>Nano-organic carbon</td>
</tr>
<tr>
<td>Abbreviations</td>
<td>Description</td>
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<tr>
<td>--------------------------------</td>
<td>---------------------------------------------------</td>
</tr>
<tr>
<td>OC</td>
<td>Open cycle</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate matter</td>
</tr>
<tr>
<td>PAH</td>
<td>Polyaromatic hydrocarbons</td>
</tr>
<tr>
<td>PCW</td>
<td>Plant cooling water</td>
</tr>
<tr>
<td>PME</td>
<td>palm methyl ester</td>
</tr>
<tr>
<td>PaSR</td>
<td>Partially stirred reactor</td>
</tr>
<tr>
<td>PLIF</td>
<td>Planar laser induced fluorescence</td>
</tr>
<tr>
<td>PoWER</td>
<td>Power, water extraction and refrigeration</td>
</tr>
<tr>
<td>RCC</td>
<td>Regenerative combined cycle</td>
</tr>
<tr>
<td>REC</td>
<td>Recuperator</td>
</tr>
<tr>
<td>RME</td>
<td>Rapeseed oil Methyl Ether</td>
</tr>
<tr>
<td>RFTE</td>
<td>regenerative feedback turbine engine</td>
</tr>
<tr>
<td>RPFR</td>
<td>Recirculating Plug Flow Reactor</td>
</tr>
<tr>
<td>SCC</td>
<td>Semiclosed cycle</td>
</tr>
<tr>
<td>SCGT</td>
<td>Semiclosed gas turbine</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
</tr>
<tr>
<td>SCNR</td>
<td>Selective non-catalytic reduction</td>
</tr>
<tr>
<td>SFC</td>
<td>Specific fuel consumption</td>
</tr>
<tr>
<td>SMD</td>
<td>Sauter mean diameter</td>
</tr>
<tr>
<td>SOF</td>
<td>Soluble Organic Fraction</td>
</tr>
<tr>
<td>SRC</td>
<td>Smokeless rich combustion</td>
</tr>
<tr>
<td>TCR</td>
<td>Thermo-chemical reforming</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>THC</td>
<td>Total hydrocarbon</td>
</tr>
<tr>
<td>UCPC</td>
<td>ultrafine condensation particle counter</td>
</tr>
<tr>
<td>UHC</td>
<td>Unburned hydrocarbons</td>
</tr>
<tr>
<td>ULSD</td>
<td>ultra-low sulfur diesel</td>
</tr>
<tr>
<td>VARS</td>
<td>Vapor absorption refrigeration system</td>
</tr>
<tr>
<td>WGC</td>
<td>Warm gas cooler</td>
</tr>
<tr>
<td>WSR</td>
<td>Well-stirred reactor</td>
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</table>
CHAPTER 1
INTRODUCTION

1.1 Background

Emissions reduction and efficiency improvement have been long-standing goals for combustion system designers. In the combustion of conventional fuels, emissions of CO$_2$, unburned hydrocarbons (UHC), CO, CO$_2$, soot particulates, NO$_x$ and SO$_x$ have been of particular concern due to their detrimental impact on health and the environment. Greenhouse gases such as CO$_2$, H$_2$O, CH$_4$, N$_2$O and chloro-flouro carbons have been found to be the major contributors to the global warming problem, and there is an unmistakable consensus that there is an urgent need to curtail the anthropogenic contribution of these gases [1]. As a result of the Kyoto Protocol, many countries are considering emissions trading and imposition of taxes on CO$_2$ generation. Several countries have taken initiatives to improve energy efficiency and harness pollution-free energy resources and technologies. Renewable energy resources like wind, hydraulic or solar energy are likely to reduce overall emissions; however, these cannot entirely meet the growing energy demand. Biofuels have been proposed as a short term solution to heightening energy and pollution crisis. Biofuel combustion is considered to reduce CO$_2$ impact on the environment, since the biomass consumes CO$_2$ in its production cycle before being used as a fuel. Using CO$_2$ sequestration and storage is another proposed CO$_2$ reduction concept. Integrated gasification combined cycle (IGCC) plants fired with biomass, are one example of reduced CO$_2$ emissions and clean combustion technology that employs gasification of biomass to produce syngas and its subsequent combustion. CO$_2$ separation can be achieved through installation of additional equipment, as in open or semiclosed combined cycle gas turbine (CCGT) plants, or chemically reformed gas turbine (CRGT) plants, where fuel is treated with steam to increase its hydrogen content and its subsequent oxy-fuel combustion [2]. Thermo-chemical reforming (TCR) may also be employed by mixing fuel with steam and insufficient oxygen, resulting in partial oxidation or mixing with recirculated exhaust
gases (containing steam from combustion products). The benefits of this include reduction in combustion irreversibility and recovery of exhaust heat [2]. Other concepts for CO₂ reduction include partial oxidation cycles and burning carbon-free fuels.

NOₓ (NO and NO₂) is another major pollutant from high temperature combustion systems, known for its deleterious effects. It forms acid rain and contributes to global warming (through production of ground level ozone) [1]. The formation of ground-level ozone due to NOₓ is also known to aggravate respiratory problems [1]. Low NOₓ systems and ultra-low NOₓ systems have been proposed with emissions below 10 ppm, and several NOₓ reduction strategies have been employed. Wünning and Wünning [3] have discussed reduction of NO through several techniques. Thermal NO can be reduced through flame cooling techniques, including injection of NH₃ or H₂O (wet NOₓ control) or cooling through exhaust gas recirculation (EGR) or cooling rods in burners (dry NOₓ control) [3]. Multistaging and usage of high velocity inlet streams are employed to cool fresh charge with exhaust products, for dry NOₓ control Wünning and Wünning [3]. Lean premixed technology [4] uses premixed air and fuel combustion with excess air for flame temperature suppression. The technology, however, suffers from problems of poor combustion stability and flashback [3]. The GE Rich-Quench-Lean technology [5] uses fuel-rich primary zone combustion, followed by a fuel-lean low temperature combustion, for thermal NOₓ reduction [6]. For reduction of fuel-bound NOₓ, reburning strategies are used for reduction of NO to N₂. Oxyfuel combustion is yet another dry NOₓ reduction technique, and has been employed in zero emissions semiclosed cycle concepts [2]. However, it suffers from drawbacks of O₂ expense, the need for the system to be air-tight, and that nitrogen-bound fuels cannot be used (such as natural gas with up to 14% nitrogen) [3]. Secondary NOₓ removal strategies include selective catalytic reduction (SCR) and selective non-catalytic reduction (SCNR). These are particularly useful for retrofitting older high emissions technologies, but may be expensive [3]. Staged combustion for NOₓ reduction may be applied by air or fuel staging (or reburning), air staging being a more effective approach
Xu et al. also suggested that NO formation in fuel-rich or reburning zones is hindered by the absence of O and the profusion of CH radicals.

SCR is a wet NO removal strategy and involves ammonia injection for reduction of NO to N. The reactions for NO removal are given below:

\[
4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O
\]
\[
2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O
\]

Particulate matter (PM) consist of very small condensed phase particles including aerosols, dust, etc. dispersed in the atmosphere, and they impact the lungs (aggravate asthma, bronchial diseases) and the heart. Particulate matter less than 10 microns and fine particles of size less than 2.5 microns are of particular concern due to the problems associated with decreased visibility. The soot particulates are typically of the order of 0.5 to 50 nm, and are a result of combustion under local fuel-rich conditions. These are predominantly composed of carbon in the form of polyaromatic hydrocarbons (PAH), known to be carcinogenic. Small sized particulates are easily ingested in the human pulmonary system, and are significant contributors to bronchial disorders and lung cancer. The traditional approach for reduction of soot emissions was that of providing adequate time, temperature and turbulence for combustion. Using hydrogen fuel combustion has been proposed as one of the means of curtailing soot and UHC emissions.

Carbon monoxide is extremely dangerous when respirated in excessive quantities, since it binds with haemoglobin and prevents oxygen supply in the blood. It is known to have detrimental effects on the heart and the nervous system. The reduction of CO, UHC and soot emissions in combustion systems, is typically achieved by increasing the residence time inside the combustion chamber, and avoiding cold-spots through efficient design. The CO, UHC and soot emissions are typically lower for fuel-lean combustion, for a range of equivalence ratios. The key problem in optimization of emissions is that, simultaneous reduction of CO, UHC, soot emissions and NO, imposes severe constraints on the system variables, and may be extremely challenging in conventional combustion systems.
However, semiclosed cycles can achieve substantially lower carbon (CO$_2$, CO, UHC and soot emissions) as well as NO$_x$ emissions, and are a key motivation behind this work.

### 1.2 Motivation

The development of power generation systems optimized for maximum power and lower overall emissions has been a prime thrust in motivating active research in the field of combustion. Several low emissions concepts have been proposed for energy systems and are actively being investigated. A novel semiclosed cycle (SCC) engine concept is being developed by an academic-industrial team lead by the University of Florida. This cycle has been successfully demonstrated in a laboratory scale engine test rig called the power, water extraction and refrigeration (PoWER) engine. This quad-generation (combined heat, power, refrigeration and water extraction) technology evolved from its predecessor engine, the regenerative feedback turbine engine (RFTE). Over and above the capability of the RFTE engine, the PoWER engine incorporates a bottoming refrigeration cycle, that is, a vapor absorption refrigeration system (VARS), that also allows fresh water harvesting.

A schematic of the PoWER system is shown in Fig. 1-1. The PoWER cycle constitutes three major components - microturbine block, turbocharger, and the VARS unit. The low-pressure compressor (LPC) and low-pressure turbine (LPT) constitute the Turbocharger. The microturbine block consists of the high-pressure compressor (HPC), combustor, high-pressure turbine (HPT) and the recuperator (REC). The VARS unit extracts heat from the EGR stream in the Generator or the hot gas cooler (HGC), and in the evaporator or the cool gas cooler (CGC). The intercooler, between the HGC and the warm gas cooler (WGC), uses the plant cooling water (PCW) to cool the EGR stream in an intermediate step. The recirculated exhaust gases pass through the HGC, WGC and the CGC, losing heat in the process. For simplicity, only the gas turbine flow path has been shown.

In order to conduct combustion experiments at high EGR, a research rig for the PoWER engine was built, known as the High Recirculation Combustion (HiRC) facility.
This system has a main air inlet (MAI) (not present in a PoWER system) that allows running the engine at high EGR in unboosted mode (without the turbocharger). Ambient air enters the cycle at State 13, flowing into the LPC. The compressed air at State 14, adiabatically mixes with the recirculated exhaust stream (State 10) at the mixing junction, the outlet of which mixes with the air (State 1) through the MAI. The MAI is generally closed for the HiRC; however, it is used when operating the engine in non-boosted mode. The mixed stream (State 2) is further compressed by the HPC to State 3, which is heated to State 3.1 in the REC, using waste heat from the exhaust gases. The heated vitiated air stream at State 3.1 enters the combustor, where the fuel is burned under overall-lean stoichiometry, to a high temperature exit State 4. The high temperature gases are expanded to State 5 in the HPT. The high enthalpy of the turbine exhaust is utilized to heat the HPC exit stream in the recuperator. In the process of heat exchange, the exhaust gases cool to State 6. A large part of the exhaust stream is recirculated back into the engine, while the remaining fraction may be exhausted through the exhaust valve (ExV) at State 18, in order to reduce the boost pressure. The exhaust at State 11, is utilized to drive the LPT of the turbocharger, and the rest of the recirculated gases (State 9, EGR stream) are used to power a bottoming VARS cycle. The HGC is the generator of the VARS unit, where a strong refrigerant solution is heated by the EGR stream to generate refrigerant vapor. The cooled EGR stream at State 9.1 then enters the (WGC), which is cooled by the PCW. Water from the exhaust products of combustion is harvested for end use, while the rest of the recirculated exhaust is fed into the CGC at State 9.2 where the liquid refrigerant further cools the EGR stream to State 9.3. The mass flow of the exhaust gas recirculation is controlled by the recirculation valve (ReV).

This study has been motivated by our interest in modeling of practical gas turbine combustors, operating on a semiclosed cycle. The SCC engines operate with part of the exhaust gases being fed back through an intermediate pressure EGR loop, to dilute the core engine reactant air stream. In earlier experimental efforts, it has been successfully
demonstrated that semiclosed cycles may have unique advantages of lower specific fuel consumption, high efficiencies at full and part loads, and lower overall emission levels. The lower combustion temperatures and fairly homogeneous distribution the reaction inside the combustor resulted in marked reduction in NO\(_x\) levels. In an effort to optimize the design of this engine configuration, several tests were conducted with varying levels of EGR. At very high levels of EGR, it was found that the flame luminosity was substantially reduced. This observation led to the hypothesis that flameless combustion is associated not only with distributed reaction, but also with significantly reduced soot formation.

In his review paper, Mansurov [9] has discussed cool sooting flames. Therein, he has cited works that have proved the existence of low-temperature thresholds of soot formation. The reduced or near-zero luminosity in the flameless regime is suggestive of low soot emissions and hence absence of radiative loss associated with the particulate black body emissions. Thus the reduced luminosity and reduced soot appears consistent with increasing EGR, as seen in our experiments. Several other research groups have reported similar phenomena, also frequently referred to as Mild combustion [3, 10]. This combustion regime has lower flame temperatures, uniform flow-field and lower pollutant levels [3, 11–14]. However, based on the observations from other researchers, there is evidence to believe that soot formation and UHC emissions may increase with EGR, especially at high equivalence ratios. As an example, Cong and Dagaut [15] investigated the vitiated combustion of natural gas/syngas mixtures through experimentation and modeling. EGR was modeled by varying CO\(_2\) composition in the oxidizer stream. Ignition delays and burned gas velocities were modeled. In their sensitivity analysis studies, it was found that, CO\(_2\) had an inhibiting effect on fuel oxidation, which could imply an increased tendency towards soot formation with increasing EGR. The combustion stability seemed to deteriorate with increasing the flow of the cooled EGR stream. It has been reported that at high levels of dilution, low C/O ratios and inlet temperatures, there is an onset of instabilities due to oscillatory combustion behavior [14]. Maruta et al. [13] showed that the
extinction limits became broader with increasing air temperature for flameless combustion. For air temperatures higher than 1300 K, the extinction limits disappeared. They also showed broadening of the reaction zone, for the case of flameless combustion. Several such contradictions exist in the growing body of literature on flameless combustion. Some of the contradictions are due to differing applications and experimental setups. For example, in their work on a sub-ppm premixed burner, Kalb and Sattelmayer [16] found that the presence of radicals had a strong effect of improving combustion stability, when the fresh stream of fuel and air was periodically admixed with the combustion products. This is an example of exhaust gas recirculation (EGR) at high temperatures (adiabatic flame temperature). In our modeling studies [11, 17] we have demonstrated that depending on the temperature of the EGR stream, the stability of combustion may actually be improved or reduced depending on its net effect on the flame temperature. Through this study, we propose to make a comparison in the soot production, combustion stability and emission levels of a semiclosed cycle operating at varying levels of EGR with the base case of a conventional open-cycle engine.

Schefer [18] studied the effect of hydrogen enrichment on flame stability and emissions on a premixed methane/air flame, under lean conditions. Measurements through the OH planar laser induced fluorescence (PLIF) technique indicated a shredded appearance close to the stability limit, and that hydrogen enrichment increased OH concentration and increased the limits of stability. It was also found that NO\textsubscript{x} and CO emissions decreased with hydrogen addition, an effect attributed to the increase in the radical pool. The increase in stability limits due to hydrogen was attributed to the wider stability limits and higher flame speed of hydrogen. This motivated us to investigate the correlation of loading parameter (LP) (measure of combustion blowout stability) with OH and CO emissions in the current study.

Duwig et al. [19] performed combustion stability studies on flameless combustion in a gas turbine combustor model, using detailed chemistry, computational fluid dynamics
(CFD) and experimental approaches. They observed that the formation and subsequent disintegration of vortical structures facilitated hot gas entrainment and improved microlevel mixing. They suggested that two non-dimensional numbers Karlowitz number $Ka_r = \left( \frac{\delta_r}{\eta_K} \right)^2 > 1$ ( $\delta_r$ is the reacting layer thickness and $\eta_K$ is the Kolmogorov length scale) and ignition number $NI = \frac{\tau_{res}}{\tau_I} > 1$ ( $\tau_{res}$ is the residence time and $\tau_I$ is the ignition delay) describe the boundaries of flameless combustion. Damkohler number has traditionally been applied as an indicator for flame stability [20], in stability models based on global chemistry [21–23]. However, in accounting for detailed chemical kinetic effects, it is incorrect to base the chemical time scale on any particular species, since the intermediate species pool serves to enhance residual reactivity. Hence, ignition delay serves as a good measure for a characteristic chemical time scale. This prompted the exploration of the correlation of LP with ignition number parameter suggested by Duwig et al. [19].

Recently, there has been a growing interest in the use of biofuels as an energy source [24], and issues involving technology readiness and fuel flexibility for combustion of biofuels. The study of alternative fuels is closely interlocked with issues of emissions. Biofuels are a diffuse energy source and hence are suitable for distributed generation [12]. Also, PoWER systems are ideally suited for distributed generation because of their fuel flexibility, high efficiency at full and part load, high compactness, and multi-generation. Due to suitability of biofuels for use in distributed generation systems, we are investigating their emissions performance in the flameless combustion regime inherent in the PoWER cycle. However, there is also concern over increased NO$_x$ emissions for biodiesel combustion, while particulate soot, CO and UHC emissions are generally lower. In addition, combustion of biofuels is of interest since combustion of biodiesel and other alternative fuels have an increased the Soluble Organic Fraction (SOF) level of particulate matter, increasing their overall toxicity [25]. Sidhu et al. [25] found that Dimethyl Ether (DME) had the highest soluble organic fraction (SOF) content of 71 %, followed by biodiesel 66 %, compressed natural gas (CNG) 38 % and diesel 20 %.
They also pointed out that biodiesel exhaust had oxygenated products like benzoic acid, pentenoic acid and various substituted methyl esters in addition to PAHs.

In one part of this study, the use of biofuels ethanol, Dimethyl Ether (DME), Methyl Butanoate (MB) in the vitiated combustion has been explored, and their combustion performance has been compared to that of n-heptane. Most biofuels are known to have lower calorific values, higher specific fuel consumption (SFC) and produce higher NO$_x$. Hence, using biofuels in the inherently low NO$_x$, PoWER cycle has the advantage of lowering overall emissions rather than potentially raising them. It has been shown that use of oxygenated fuels has a pronounced effect of reducing soot formation [26]. However, inconsistent results have been reported for the combustion of biofuels in the vitiated combustion regime. The emissions performance depends on the source and type of biofuel, and involves interaction of competing effects of fuel properties and combustor system design parameters. Through this modeling effort, clarification is sought on how EGR can improve or adversely affect emissions performance, depending on the operation regime specified by parameters such as equivalence ratio, residence time, EGR level and EGR temperature. This study investigates the problem using a simplified model from the perspective of detailed chemical kinetics, in order to resolve the inconsistencies observed in combustion performance of biofuels in the vitiated combustion regime.

1.3 Research Objectives

Preliminary studies have been carried out to investigate the key issues involved in flameless combustion, and to define clear objectives of the project. In order to study the performance of biofuels in vitiated combustion regime, the combustor was modeled using a simplified reactor network, with a partial recirculation of the exhaust flow. Detailed chemical kinetic simulations were performed to compare the pollutants generation and blowout characteristics during combustion under varying conditions of exhaust gas recirculation and equivalence ratios, and a comparison was made with combustors
operating on a conventional cycle. Based on the insight gained from the preliminary studies, the following objectives of the research study were set:

- **Research Objective 1.** Comparison of biofuel performance in vitiated combustion
  - To study and compare the combustion efficiency, pollutant emissions generation (in terms of CO and UHC) and flame blowout stability of various biofuels namely, ethanol, methyl butanoate (biodiesel fuel surrogate) and dimethyl ether, with respect to n-heptane (diesel fuel surrogate).
  - To investigate the performance (emissions, combustion efficiency and stability) of CO/H\textsubscript{2} syngas mixtures (25%, 50% and 75% H\textsubscript{2}), and present a comparison with conventional methane fuel.
  - To study the effect of EGR on biofuel emissions and stability, at a fixed EGR stream temperature, in comparison to the zero EGR open cycle (OC) case.

- **Research Objective 2.** Modeling combustion stability
  - To investigate flame blowout stability for vitiated combustion at fixed fuel composition (ethanol fuel), for varying EGR, equivalence ratios, residence times and EGR stream temperatures.
  - To investigate the correlation of loading parameter with OH concentration.
  - To investigate the correlation of loading parameter with ignition number (ratio of ignition delay and residence time).

- **Research Objective 3.** Modeling soot formation
  - To predict the combustion efficiency and pollutants generation, in terms of CO, UHC, soot precursors with varying residence times, equivalence ratio, EGR and EGR temperature.
  - To model the effect of EGR on the formation soot particulates and present a comparison with the zero EGR OC case.
  - To compare results of soot formation model developed by Frenklach and coworkers, and that developed by Richter et al. (Howard and coworkers).
Figure 1-1. Schematic of a Power, Water Extraction and Refrigeration Cycle Engine
CHAPTER 2
LITERATURE REVIEW

2.1 Semiclosed Cycle Engines and the Power, Water Extraction and Refrigeration (PoWER) Engine

Semiclosed Cycle (SCC) engines are a novel concept that have regained attention due to technological advances over the last couple of decades. The SCC concept was first proposed back in the 1940s. The early investigations were carried out by Anxionnaz [27, 28], Davis [29], DeWitt and Boyum [30], Gasparovic [31, 32]. An SCC engine utilizes exhaust gas recirculation (EGR) at intermediate pressure [33]. This presents a unique combustion environment, which has been investigated through modeling, for emissions reduction [11, 12, 34–37] as well as thermodynamic cycle optimization [35, 38–41]. Several variations of this concept have been suggested [2], including those investigated at the University of Florida. The Regenerative Feedback Turbine Engine (RFTE) configuration was one variant of the SCC concept, with a turbocharged-intercooled-recuperated cycle developed at the University of Florida (UF). Subsequently, the High Pressure Regenerative Turbine Engine (HPRTE) configuration was developed, which was a combined cycle concept. Initially a bottoming Rankine cycle was proposed, which was eventually substituted by a bottoming refrigeration cycle. This led to the conception of the PoWER engine with capabilities of quad-generation (combined heat, power, refrigeration and water extraction).

The HPRTE engine was inspired by the Wolverine engine built as a backup system for nuclear propulsion systems for submarines in naval applications. Eventually, Project Wolverine was discontinued due to the success of the nuclear program [39]. Laganelli et al. [42], in their white paper, outlined the benefits of the HPRTE system for naval applications. They suggested that the capability of fresh water extraction from combustion gases, reduced thermal signature, lower stack sizes, higher power density and high part-load efficiency, made HPRTE systems particularly suitable for naval applications. In another study, Meitner et al. [43] showed that the HPRTE engine in open cycle mode,
produced CO concentration of 124 ppm and NO\textsubscript{x} concentration in the range of 53 to 65 ppm. In semiclosed cycle mode, they demonstrated that, the CO emission levels were drastically reduced to values as low as 5 ppm. They attributed the reductions in emissions to lower exhaust flow rates, dilution of combustor primary zone with product gases, oxygen depletion and lower flame temperatures.

The HPRTE was derived from the RFTE concept by including a bottoming refrigeration cycle to a turbocharged-intercooled-recuperated semiclosed cycle of the RFTE. In a quest to unravel the complexities of vitiated combustion, several combustion modeling studies were undertaken [11, 23, 34, 36, 37, 44]. Muley and Lear [34] investigated the thermal NO\textsubscript{x} emissions performance of the SCC engines through modeling. The combustor primary zone was analyzed using a perfectly stirred reactor (PSR) model, and the NO\textsubscript{x} chemistry was modeled using the Zeldovich mechanism. The significant NO\textsubscript{x} emissions reductions achieved in SCC systems were attributed to lowering of the flame temperature and oxygen depletion, as a result of dilution with an externally cooled EGR stream. Crittenden et al. [23, 37] modified the PSR theory to predict the combustion stability and emissions performance of an engine operating on SCC. The approach of Strehlow [21] was extended, in his work, to predict combustion performance for SCC engines. Harwood et al. [36, 44] studied the semiclosed cycle combustor performance using recirculating plug flow reactor (RFPR) model, to account for internal recirculation. They demonstrated that flame stability was a strong function of internal recirculation flow and the residence time in the combustor. Further, it was shown that, the amount of internal recirculation required to maintain stability increased with decreasing temperature of the inlet stream.

Thermodynamic analysis of SCC engines is a challenging problem, and several studies have been conducted to understand the impact of several design parameters [35, 38, 40, 41, 43]. MacFarlane and Lear [38] investigated the benefits of reinjection of extracted water from a RFTE system. They concluded that reasonable performance improvements in terms of increased efficiency, decreased specific fuel consumption (SFC), and increased
specific power could be achieved from RFTE engine by means of water injection. It was found that the optimum configuration for the most practical system was achieved for the case of water extraction matching water injection, so that there is no external storage requirement and a simpler control scheme can be used. Meitner et al. [39] demonstrated the HPRTE SCC concept on a turboshaft gas turbine engine. They suggested that an HPRTE engine had benefits of reduced air flow, lower burner temperature, compactness, flat SFC curves and low emissions. Their analysis predicted a constant specific fuel consumption as a function of power and their experimental observations showed a significant reduction in emissions.

Boza et al. [45] performed a thermodynamic analysis of a combined cycle SCC engine with vapor absorption refrigeration as the bottoming cycle, the first study of the PoWER cycle. They inferred that the thermal efficiency and refrigeration ratio were strong functions of turbine inlet temperature and the ambient temperature, respectively. Two cases, of a small and a large engine were analyzed, both of which showed 2 to 5 points increase in combined thermal efficiency (inclusive of the refrigeration power).

Nemec and Lear [35] demonstrated via a design point study that an HPRTE cycle with a bottoming rankine cycle showed significant improvements in efficiency. A variant of the HPRTE with a vapor absorption refrigeration system (VARS) bottoming cycle was eventually developed [46]. During the course of its development, several technological innovations took place. It was found that an SCC engine such as the HPRTE was capable of producing fresh water. Khan et al. [40, 46–51] investigated the performance of the HPRTE engine through modeling and experimentation on an HPRTE test facility. It was also found that these engines are capable of running in flameless combustion mode, at high levels of EGR. The newest variant of the SCC engine, being developed at UF, is known as the PoWER engine. In recent modeling studies [41, 52], the PoWER engines with multi-evaporator configurations of the VARS have been investigated for ice production, that may be used for load-leveling.
Khan et al. [40] studied the water extraction performance of PoWER cycle engine. They concluded that increasing turbine inlet temperature increased efficiency, while decreased refrigeration ratio and water extraction, on the other hand. Recuperator inlet temperature had an optimal effect on efficiency and refrigeration, while it enhanced water extraction. Increasing low-pressure compressor (LPC) pressure ratio adversely affected efficiency, while improved refrigeration ratio and water extraction.

Camporeale and Fortunato [53] studied a semiclosed gas turbine cycle operating with high temperature dilute combustion through EGR. A bottoming steam cycle was considered for combined cycle gas turbine systems. They suggested that such a cycle had the advantages of reduction of combustion exergy losses due to high oxygen stream preheat, compact heat exchangers due to higher system pressures, high part load efficiency and appropriate conditions for CO₂ separation.

Fiaschi and Manfrida [54] investigated the semiclosed gas turbine (SCGT)/regenerative combined cycle (RCC) concept, as a potential zero CO₂ emissions system. This cycle includes intercooling, aftercooling, recuperation, water extraction and re-injection gas cycle, with a bottoming rankine cycle. They concluded that drastic reductions in the cost and size of HRSG of the bottom rankine cycle could be achieved.

Jordal et al. [55] modeled the performance of oxyfuel combustion with CO₂ dilution during high temperature combustion in a semiclosed cycle, including the effect of cooling of turbine blades. They found a deterioration of turbine performance and increase in turbine speed for fixed geometry. The improvement of efficiency achieved through modification of the turbine blade angles, was indicative of the need for redesigning the turbine for oxyfuel combustion.

Bolland and Mathieu [56] compared two CO₂ reduction strategies, one with oxyfuel combustion, with recirculation of CO₂, and the other a semiclosed brayton cycle with CO₂ sequestration. They highlighted that the benefit of the oxyfuel semiclosed cycle was that, it does not require additional CO₂ separation equipment, however, an air separation
unit (ASU) is required. It was found that the cycle with CO₂ sequestration had higher efficiency in comparison to the oxyfuel combustion cycle, for all recirculation rates.

### 2.2 Flameless Combustion

Flameless combustion is a recently observed phenomenon, that holds huge potential in improving combustion performance and emissions reduction [10]. The reported benefits of flameless combustion include uniform temperature field and species concentration profiles, significant NOₓ reductions, lower soot yields and noise levels [3, 10–13, 57]. A significantly higher level of homogeneity of temperature and concentration profiles is achieved, suggestive of a regime shift from a diffusion controlled regime to that of kinetic control [58]. The absence of temperature peaks results in lower NOₓ, while the absence of cool pockets reduces zones of frozen reaction chemistry and high CO emissions associated with it. Several names have been proposed for the phenomenon of flameless combustion by researchers across the globe. In Japan, the phenomenon has been referred to as excess enthalpy combustion, that is now referred to as HiTAC/HTAC [59, 60]. The HiTAC technology utilizes oxygen depletion in conjunction with heat regeneration to achieve flameless combustion. The term moderate and intensive low oxygen diluted (MILD) combustion is used in Italy [14, 53] and flameless oxidation (FLOX®) in Germany [3]. Other names such as distributed colorless combustion, volumetric combustion, green flame combustion, and diluted combustion [61] refer to the same phenomenon. Mild combustion can be achieved as a result of intense internal mixing and oxygen dilution as in case of FLOX® technology [62] or through external exhaust gas recirculation [11, 12, 17, 46, 53, 63–65]. Internal adiabatic EGR achieved through hot gas entrainment has also been utilized in the Integral Low NOₓ Injection (LNI) burner technology (United States Patent 6206686, See http://www.freepatentsonline.com/6206686.html) and LTC in diesel engines [66]. Several researchers [7, 61, 67–71] have studied flameless combustion in multi-staged burners and found improved combustion performance. The NOₓ reductions in
flameless combustion have been also investigated through modeling, by several researchers [44, 72, 73].

There are many predictive indicators that may be used to define transition from conventional combustion regime to flameless combustion. Cavaliere and de Joannon [74] suggested that flameless combustion condition is achieved when the inlet reactant temperature is larger than the auto-ignition temperature and the ignition delay is longer than the mixing time, so that a distributed volumetric combustion is achieved. Derudi et al. [75] used the condition of drastic reduction in NO as the condition for attainment of flameless combustion. Kumar et al. [76] investigated the homogenization of gradients through temperature-volume and O$_2$-volume cumulative distribution functions as the criterion for attainment of mild combustion. Aceves and Flowers [77] used examination of soot precursors to identify regimes for flameless combustion. Other researchers have noted a marked reduction in OH concentration (strongly correlates with heat release rate [77]) in flameless combustion [10] through chemiluminescence and planar laser induced fluorescence (PLIF) studies, which may be used as a criterion for the transition to flameless regime.

In diesel internal combustion (IC) engines the flameless combustion concept is utilized for achieving non-sooting combustion through two regimes of smokeless rich combustion (SRC) and modulated kinetics (MK) [77]. The soot formation process is normally predominant in the temperature range between 1600 and 2600 K and at equivalence ratios greater than 2 [77]. Glassman et al. [78] investigated critical sooting temperatures and found that soot formation inception typically begins at around 1600 K, irrespective of the fuel. Hence a temperature boundary may be identifiable for transitioning to flameless regime. The transition to flameless combustion is usually abrupt [11, 12, 17], and accompanied by a sudden drop in flame luminosity and homogenization of the gradients in temperature and concentration profiles inside the flow field. The boundaries of transition to flameless combustion may be correlated with onset of the soot formation process [64]. Derudi et al. [75] used NO$_x$ emissions below 30 ppm and CO below 50 ppm, as the
criterion for transition to flameless combustion. The NO\textsubscript{x} emissions reductions in flameless combustion are mainly due to reduction in thermal NO\textsubscript{x} formation. Since the fuel-NO\textsubscript{x} route is less sensitive to temperature, EGR has little impact on its reduction \cite{70}.

Combustion processes have traditionally been classified into preflame combustion, deflagration and detonation \cite{6}. Preflame combustion is typically slow and distributed volumetrically and takes upto 100 s for 80% completion \cite{6}. Deflagration is a faster combustion process occurring at a flame front and takes upto 1 ms for 80% completion \cite{6}. The deflagration waves typically travel at under 1 m/s, while detonation waves travel at supersonic velocities \cite{6}. Gas turbine combustion typically proceeds in the deflagrative regime. One possible categorization measure of flameless combustion could be the switch from deflagrative to volumetric combustion. The Klimov-William criterion \(l_k < \delta_L, U' \geq S_L\) where \(l_k\) is the Kolmogorov microscale and \(\delta_L\) is the laminar flame thickness \cite[229]{79}) must not be satisfied for distributed reaction to occur \cite{75}. This typically occurs at low Damkohler numbers \cite{80}, with high turbulence intensities and EGR. The excess enthalpy ratio, defined as the ratio \(\frac{T_{ad} - T_{in}}{T_{in} - T_{ref}}\) \cite{81}, is found to be lower for flameless combustion, and may be used as an indicator for predicting the boundary of flameless regime. For stability, the inlet temperature should preferably be higher than autoignition temperature \cite{81}.

Flamme \cite{68} has investigated the use of FLOX\textsuperscript{®} and continuous staged air combustion (COSTAIR) burner technologies as a NO\textsubscript{x} reduction strategy for glass furnaces. While a staged burner had a primary air stream, a flameless oxidation burner did not have it. They concluded that, with flue-gas recirculation, low NO\textsubscript{x} emissions were possible even with higher air preheating. The NO\textsubscript{x} emissions were under 200 mg/m\textsuperscript{3} for inlet air preheat temperatures upto 1000 C and furnace temperature of 1200 C while the standard burner produced NO\textsubscript{x} emissions upto 1500 mg/m\textsuperscript{3} for similar conditions. The uniform temperature field of these approaches allowed increase of furnace chamber temperature. They also investigated the effect of fuel bound nitrogen in combustion of natural gas with
O₂ and flue-gas recirculation. Flamme [82] explored the use of flameless oxidation (FLOX) and COSTAIR burner technologies for gas turbine combustion and compared them against the lean-premixed combustors.

Shaddix et al. [83] studied premixed combustion of methane and various mixtures of syngas, and oxygen stream diluted with CO₂ in a swirl stabilized combustor. The oxy-fuel concept is a frequently employed CO₂ removal strategy, used in integrated gasification combined cycle (IGCC) plants. Significant reduction in NOₓ was found although the CO emissions were still high. They reported that the increasing H₂/CO ratio of syngas improved flame stability substantially. They highlighted that lean premixed combustion had the drawbacks of reduced flame stability and rise in CO emissions at low equivalence ratios, while NOₓ emissions reduced as a result of reduction in flame temperatures. The CO emissions were high for φ > 0.95 and φ < 0.40 [83]. The combustion efficiencies dropped significantly for equivalence ratios below 0.4, for all cases.

Weber et al. [70] studied the use of flameless combustion technology for combustion of gaseous, liquid as well as solid fuels in furnaces. A precombustor added before the furnace, was used to supply high air preheat, and a hot gas recirculation stream was developed through a reverse flow caused by the high momentum of inlet fuel stream [70]. They found that upto 60-70 % reductions in NOₓ were possible by application of low NOₓ burner technology with fuel or air staging. They attributed lower NOₓ emissions in coal combustion as compared to natural gas, light fuel oil and heavy fuel oil, to NOₓ reburning and longer residence times. They found that for liquid firing, high particulate emissions were substantially reduced by reoptimization of the atomizers for flameless combustion. In addition, they observed uniform furnace heat flux, reduced gradients and marked reduction in NOₓ levels.

Aida et al. [69] investigated the multistaging of lean burn combustors to burn prevaporized kerosene-air mixtures. They found that very high combustion efficiencies
and ultra-low NO\textsubscript{x} could be achieved by multistaging. They also observed existence of NO\textsubscript{x} reburning effects even under multistaged lean-lean conditions.

Levy et al. [65] investigated the thermodynamics of the FLOXCOM high temperature flameless combustion process with admixing. It was demonstrated that for a fixed combustion exit temperature, the oxygen concentrations remained close to stoichiometric, while a 100 % primary zone combustion efficiency was assumed.

Kajita et al. [71] showed the use of flameless combustion through burner multistaging for dry NO\textsubscript{x} reduction. Lean premixed combustion, frequently employed for dry NO\textsubscript{x} reduction, had the drawback of reduced flame stability and low combustion efficiency at very lean conditions. As a result, the air-fuel ratio had to be more tightly controlled. In the multistaged concept, in addition to the eight premixing combustors, a second stage pilot diffusion burner was used, that enhanced stability at very lean conditions at low loads. They found the existence of NO\textsubscript{x} reduction process during multistaging.

Gupta and Hasegawa [84] examined the effect of increased air preheat and dilution on the overall combustion performance and flame structure of propane air diffusion flames. Their results indicated that at high levels of dilution and preheat, the flame had reduced gradients in temperature and concentrations, and low emissions and luminosity. Preheating increased flame volume (due to lower diffusion rates as a result of lower density), while increasing oxygen concentration (decreasing dilution) had the opposite effect. The ignition delay was found to decrease with increasing air preheat and increase with the amount of dilution. The emissions spectra showed increasing OH, CH, C\textsubscript{2} and H\textsubscript{2}O emissions with increased air preheat. Increasing air preheat facilitated flame stabilization despite the reduced oxygen levels [10]. At high preheat and oxygen depletion, propane fuel produced green colored flame due to high levels of C\textsubscript{2} species [10]. A further reduction in oxygen concentration, led to discoloration of the flame. High radiative and convective heat fluxes were observed due to high flow velocities, as well as increased
wall heat flux [10]. The flame stand-off distance, decreased with increasing air preheat, indicating reduced ignition delay and improved flame stability [10].

Kumar et al. [76] investigated scaling approaches for a mild combustion burner. It was found that secondary air injection positioning and injection velocity had significant impact on exhaust recirculation. They evaluated traditional scaling methods of constant velocity, constant residence time, etc., and found those to be inadequate for mild combustors. They found that constant velocity approach increased mixing time and reduced mixing rate while the other approaches led to increased system pressure drop. They introduced an additional scaling criterion based on the convective time scale (D/U) being less than 80 μs.

Ellul et al. [85] studied the effect of fuel compositions in highly preheated air combustion in counterflow diffusion flames. They found that NO formation was suppressed, and that NO reburning and N₂O routes become predominant for flameless combustion.

Mancini et al. [86] investigated natural gas flameless combustion in a furnace, with air preheat at 1300 C. They concluded that NOₓ formation was predominantly through the thermal route and that NO-reburning was insignificant. This is in contradiction with the work of Schutz et al. [62], Nicolle and Dagaut [87].

Adachi et al. [67] investigated diluted multi-staged combustion in three-staged combustor. The primary axial flow stage was used to stabilize the combustion of secondary and tertiary cross flow stages. NO from the primary stage was found to be completely oxidized to NO₂ in the subsequent stages. They also reported substantial reduction in combustion oscillations with multistaging. The impact of biomass composition variance was addressed by diluting CH₄ mixtures with varying amounts of CO₂. Low NOₓ and high combustion efficiency was observed in the temperature range between 1500 to 1700 K.

Nicolle and Dagaut [87] modeled chemical kinetics of CH₄ flames to study NO-reburning phenomenon in flameless combustion. They discussed the significance of the N₂O route,
and the reduction of NO by hydrocarbon radicals under flameless combustion conditions. They found partial conversion of NO into HCN and subsequently NH$_3$ occurs, during autoignition of the mixture. The presence of the exhaust H$_2$O was found to inhibit prompt-NO and NNH routes. In the post-ignition phase, the thermal and N$_2$O routes were favored, while NO reburning may be prevalent under fuel-rich conditions [87].

Wang et al. [8] performed techno-economic studies to compare selective catalytic reduction (SCR), COSTAIR and FLOX® technologies for NO$_x$ reduction. The COSTAIR burner has two air streams, primary and secondary, while the FLOX® technology has no primary air supply [8]. However, both technologies rely on entrainment of exhaust gases into the reactant stream for temperature reduction. They concluded that the use of the non-standard COSTAIR and FLOX® burners had high efficiencies of NO$_x$ removal, with lower system capital cost and electricity selling price.

Blasiak et al. [81] investigated flameless air and oxyfuel furnace combustion. They found that oxyfuel combustion had very low NO$_x$ due to the absence of N$_2$. Lower flame temperatures, larger volume and uniform temperature distributions were observed with oxyfuel combustion. A simple radiation heat transfer model, predicted the flame volume to be an inverse fourth power function of temperature. Flame volume was predicted using gas sampling and calculating a local oxidation mixture ratio, and found to be larger for the case of oxyfuel combustion.

The flame blowout stability in the regime of flameless combustion has competing effects due to the effect of dilution of the inlet stream and its temperature. While the increase in inlet temperature promotes flame stability, the inlet dilution has just the opposite effect. The flame stability for vitiated combustion may also be improved with hydrogen addition. The work of Derudi et al. [75] discusses the use of non-conventional fuels such as coke-oven gas, with hydrogen promoting flame stability.

Hamdi et al. [88] investigated the pollutant emissions in gas turbine systems at high pressures and temperatures, through detailed kinetic modeling in a reactor network with
two PSRs. They found that at low pressures all three routes – Zeldovich, Fennimore and N₂O mechanisms were of equal significance, while at higher pressures N₂O route was dominant. The overall NOₓ emissions increase slightly with increasing pressure [88]. They also found a slight drop in CO emissions with increased pressures, and highlighted the reductions in CO₂ emissions as a result of reduced exit mass flow due to EGR.

Katsuki and Hasegawa [60] defined highly preheated air combustion (HPAC) as combustion with inlet reactant temperature above autoignition temperature, so that combustion proceeds spontaneously, within the combustion chamber even in the absence of an ignition source. Flame stabilization through use of a bluff body or recirculation are not necessary for such a case [60]. They reported the possibility of considerable reduction of furnace size and fuel consumption with the use of this technology.

Xu et al. [7] investigated staged combustion for NOₓ reduction. They concluded that staged combustion in primary, reburning and burnout zones is an effective strategy for NOₓ reduction. They also pointed out that H₂ and C₂H₂ fuels had good NO reburning efficiency. CH₄ addition had a positive effect while CO addition did not impact NO reduction. They found that the intermediates C, CH, CH₂ and HCCO substantially contributed to the reduction of NO.

Characterizing the flame structure in flameless combustion has been of interest to researchers, and both experimental [89] and numerical approaches [19, 61, 62, 90–94] have been applied. Zero-dimensional analysis on flameless combustion has been applied for detailed chemical kinetic studies, to predict flame stability [14, 58], and emissions [77, 87, 88].

Fuchihata et al. [89] investigated flame structures for flameless combustion using laser tomography, chemiluminescence, laser dopler velocimetry (LDV) and temperature measurements. They observed the boundary of transition between distributed combustion regime and that where wrinkled flames begin to appear. They noticed that distributed reaction zone occurs when a reaction is initiated within a low Damkohler number zone,
while propagation of a laminar flame into a low Damkohler number zone led to the formation of a thin reaction zone.

Piepers et al. [93] performed experiments and computational fluid dynamics (CFD) modeling of natural gas flameless combustion in a furnace. They found that the minimum safe operation temperature for the furnace was 700°C under normal flame mode, while 800°C for flameless mode. The stability was found to deteriorate, on reconfiguring the positioning of primary and secondary nozzles. They also highlighted that as a result of slow kinetics of flameless combustion, the ‘mixed is burned’ assumption, frequently used in CFD modeling, does not hold true under low load conditions.

Galletti et al. [90] performed CFD analysis of a burner operating under MILD combustion regime. The results of two numerical models, a 3D and an axisymmetric model, were compared with the experimental data. Their results suggested that the axisymmetric model, that did not include details like the recirculation windows, was too simplistic and inaccurate. They found a significant NO\textsubscript{x} reduction. The turbulent damkohler number for higher internal recirculation, achieved through decreasing air flow velocity, was lower than that for combustion in flame mode [90]. Hence, turbulence-chemistry interaction was significant in MILD combustion [90].

Tabacco et al. [94] investigated the flameless combustion process, through CFD and zero-dimensional detailed kinetic simulations. They found that with the increase in recirculation stream temperature, the ignition delays reduce and turbulence-kinetics interactions become stronger. The strong turbulence-kinetics (Da = 1, comparable time scales) interactions result in lower NO\textsubscript{x} and increased homogeneity. On the other hand at lower recirculation temperatures, the reaction was predominantly found to be kinetically controlled [94]. Increased CO\textsubscript{2} and H\textsubscript{2}O in product gases, increase radiation absorption assisting reactant autoignition and promoting thermal homogeneity (thermal effect) [94]. The mass effect of recirculation (dilution) is that of slower kinetics and weakening of heat release [94]. The kinetic effect associated with recirculation was that of increased H and
OH radicals while decreased O radicals, due to the presence of higher H₂O content, and altered NOₓ formation chemistry [94]. The overall NOₓ was found to be suppressed due to reduced O radicals and reduced flame temperatures. The predominant NOₓ formation route was found to be that of nitrous oxide (N₂O), prompt NOₓ being negligible, while the thermal NO and NO₂ routes contributed a fairly large proportion of the total NOₓ [94].

Schutz et al. [62] used partially stirred reactor (PaSR) model to study the NOₓ generation in a FLOX® combustor. They found that for the flameless oxidation process, NO production through the routes of Zeldovich, Fennimore and N₂O mechanisms were of the same order of magnitude. They also highlighted the inadequacy of the PaSR and $k - \epsilon$ models to capture the turbulence/chemistry interactions well.

Awosope et al. [61] used CFD modeling of flameless oxidation to study its application to gas turbine combustors. They compared their numerical modeling results to those of an experimental facility comprising of a premixer, precombustor and an after-burner. Their results demonstrated reductions in NOₓ and improved pattern factors in gas turbines.

Coelho and Peters [91] used Eulerian particle flamelet model (EPFM) (an unsteady flamelet approach) to predict NO formation. They found satisfactory agreement between their model and experiments, while the steady flamelet approach, on the other hand, was found to overpredict their measurements.

Yuan and Naruse [92] performed CFD analysis and experiments on furnace mild combustion. They compared the performance of diluents N₂, CO₂, and He in flameless combustion and found CO₂ produced lower flame temperatures, compared to He and N₂. They ruled out the possibility of the difference being purely a result of thermal effects, since N₂ and CO₂ had comparable heat capacities. They quantified homogenization of temperatures as a function of the ratio $\frac{T_{\text{max}}}{T_{\text{mean}}}$, and found improved homogenization with decreasing oxygen concentration in presence of highly preheated air. They used Tesner’s two step model for soot formation, and found maximum soot concentrations to be higher with higher preheat temperatures. At high preheat, the soot maximum concentration
was higher with lower O_{2} \% (increased dilution) \cite{92}. They found OH concentrations to decrease with increased dilution and air preheat. They also determined the optimum temperatures and oxygen concentrations for NO_{x} reduction.

Marek and Tacina \cite{95} investigated effect of adiabatic EGR in a flame tube combustor and found improvements in NO_{x} and efficiency. They also found higher range of operability in equivalence ratio (at higher efficiency) with increasing EGR. Additionally, they found that NO_{x} may also increase with increasing EGR, especially at higher equivalence ratios, and attributed these to heterogeneities of spray combustion. The NO_{x} dependence on residence time was reduced with increasing EGR \cite{95}. Moreover, they found that air-quench rates and lower flame temperatures had a strong effect on NO_{x} reduction.

\textbf{2.2.1 Effect of Diluent Gas}

CO_{2} has been found to have strong retarding effect kinetically \cite{15, 15, 92, 96} on fuel oxidation. H_{2}O has a positive kinetic effect due to the increase in H and OH radicals \cite{39}. The diluent gases, N_{2}, CO_{2} and H_{2}O, have a strong thermal quenching effect, while the effect of N_{2} has been found to be purely thermal \cite{15}.

Cong and Dagaut \cite{15} investigated the vitiated combustion of natural gas/syngas mixtures through experimentation and modeling. EGR was modeled by varying CO_{2} composition in oxidizer stream \cite{15}. It was found through sensitivity analysis, that CO_{2} had an inhibiting effect on fuel oxidation.

Levy et al. \cite{97} studied ignition delays for diluted methane mixtures in shock tube studies and modeling efforts. They reported the insensitivity of ignition delay measurements to the diluent composition by comparing the cases of CH_{4} - N_{2} and CH_{4} - N_{2}/CO_{2}/H_{2}O mixtures. They’ve also highlighted that the inhibition of combustion by CO_{2} reported by Cong and Dagaut \cite{15}, Lisianski et al. \cite{96}, could not be confirmed through their simulation or experiments.
Macadam [98] studied the effect of diluents in vitiation combustion in jet-stirred reactor (JSR). Both N₂ and CO₂ vitiation was found to reduce sooting, and CO₂ seemed to enhance oxidation of the soot particles (through increase of OH radical pool by the reaction \( CO₂ + H → CO + OH \)) [98]. The effect of flame temperature, and dilution at constant flame temperature were also investigated. Similar studies were conducted by Hui et al. [99], to study the influence of dilution on flame structure and emissions from a counterflow diffusion flame of syngas. They found increase in CO and decrease in NO with dilution at constant flame temperature. They found that N₂ and CO₂ enhanced, while H₂O suppressed NO emissions.

Wilson and Lyons [100] investigated the flame liftoff and stability of methane and ethylene flames in coflow configuration, with N₂ dilution. They found reduced jet velocity and coflow velocity at a given flame height, were needed when dilution and coflow velocity were increased. They also found that dilution impacted flow conditions more strongly than the chemistry. Derudi et al. [75] found an upper limit in dilution ratio existed, beyond which poor combustion efficiency and high CO emissions resulted, due to a significant reduction in O₂ concentration.

### 2.2.2 Role of Autoignition Temperature

The importance of auto-ignition temperature in flameless combustion has been discussion by Joannon et al. [14, 58], Katsuki and Hasegawa [60], Blasiak et al. [81], Tabacco et al. [94]. Inlet reactant temperatures above the auto-ignition temperature has been found to help stabilize flames even at high dilution levels. High dilution levels and temperatures, and the presence of CO₂ and H₂O increases radiative loss, assists reactant autoignition and promotes homogenization of temperature [94].

### 2.2.3 Effect of Vitiation on Soot Formation

Macadam [98] studied the effect of diluents in vitiated combustion in a JSR. Both N₂ and CO₂ vitiation were found to reduce sooting, and CO₂ seemed to enhance oxidation
of the soot particles (through increase of OH radical pool by the reaction $CO_2 + H \rightarrow CO + OH$) [98].

Kowalik et al. [101] showed that soot formation in liquid fueled JSRs is markedly different from gas fueled. They tested spray combustion of toluene and iso-octane fuels and found sooting levels dependent strongly on the spray characteristics. Toluene produced much greater soot emissions compared to iso-octane. Combustion of ethylene and iso-octane (premixed and prevaporized) fuels in the JSR resulted in observable soot formation for equivalence ratios greater than 2.4 (at 7 ms residence time) [101]. They found opposite trends in soot generation as functions of temperature, when liquid and premixed combustion methods were applied. The premixed flames produced less soot at higher temperatures while the liquid droplet combustion resulted in the opposite trend, resulting from unmixedness typical of diffusion flames [101]. This might be significant in explaining results from the experiments on the PoWER engine, since the PoWER engine was operated in heterogeneous vitiated combustion mode, with a corresponding reduction in temperature and sooting.

Joannon et al. [58] studied the process of dilute combustion of methane under fuel-rich conditions. They studied the effect of C/O ratio and inlet temperature on flameless combustion. They found that the inlet flow dilution could be correlated with the reduction in acetylene formation. They suggested that the partial oxidation due to the inlet oxidizer stream as well as from $CO_2/O_2$ reduction is the cause for low luminosity and increased homogeneity in flameless combustion. They found that the flameless combustion is similar to a two-stage oxidation process and that the unusual properties in the regime were due to the staged process and well-stirring in the oxidative-pyrolytic condition.

Aceves and Flowers [77] predicted chemical composition and soot precursors in the process of fuel-injection in diesel engines using detailed chemical kinetic simulations and simplified mixing. The soot precursor generation was demonstrated to be a function of equivalence ratio at the time of ignition, which is a strong function of mixing times and
combustion temperature. EGR was found to increase the soot precursor formation to maximum and then decrease (towards stoichiometric mixture conditions) [77]. In the SRC, the air entrainment into the injected fuel stream is controlled to low amounts lowering the combustion temperature, and hence reducing soot formed. In the MK approach the mixing rates are enhanced while the operating temperature is reduced, to avoid ignition until low equivalence ratios are not achieved.

Yuan and Naruse [92] found maximum soot concentrations to be higher with higher preheat temperatures. Further, they found that at high preheat, the soot maximum concentration was higher with lower O$_2$ % (increased dilution).

Huth and Leuckel [102] studied soot formation in turbulent plug flow reactor using natural gas as a primary fuel and propane as a secondary fuel and for varying hot gas temperatures (1273-1773 K), residence times (30-40 ms) and secondary fuel concentrations. The setup was similar to a multistaging concept and hence indicative of vitiation. The primary zone temperature was varied between (1733-1253K) by preheating air. They observed decrease in soot growth rates at high temperature, similar to premixed laminar flames. They defined the inception point as the point where soot volume fraction exceeds $10^{-10} \text{ms}^{-1}$ at a soot volume fraction of $4 \cdot 10^9$ at 40 ms.

Pischinger et al. [103] studied soot formation in diesel engines. They also reported results of soot formation in vitiated environment (fuel-rich natural gas combustion products). They found a critical sooting temperature of 1450 K, under high pressure vitiated combustion conditions, as opposed to lower critical temperatures in shock tube experiments.

### 2.2.4 Stability in Flameless Combustion

Vitiated combustion inherently is prone to instability due to dilution of the reactants. Since the technology of vitiated combustion is fairly new, combustion systems still need to be optimized for this regime. Several studies have been performed to understand combustion stability in vitiated combustion [3, 10, 11, 14, 17, 19, 21–23, 37, 44, 57, 65, 57].
Some of these efforts were based on global reaction kinetics, including the stability studies on conventional systems and fuels [21, 22, 106–110].

Yuan and Naruse [92] performed CFD analysis and experiments on furnace mild combustion. They found OH concentrations to decrease with increased dilution and decreasing air preheat. Since OH emissions have been found to correlate with flame stability [18], these results would be indicative of the functional dependence of stability on dilution and EGR temperature. It would also be relevant to point out that, although the motivation of this work has been in determining the limiting EGR at the blowout condition, Derudi et al. [75] have found that an upper limit in dilution ratio existed, beyond which poor combustion efficiency and high CO emissions resulted, due to a significant reduction in O2 concentration.

In well-stirred reactor (WSR) studies on lean blowout, Sturgess et al. [104] proposed a nitrogen diluent technique to determine the blowout limits at subatmospheric conditions (for aircraft engines). Their correlated blowout predictions showed loading parameter (LP) variations by 1 to 2 orders of magnitude, for various blowout equivalence ratios.

Studies have been performed on classification of the flameless combustion regime [75, 105], and these in some respect, are associated with the blowout stability limits of the regime. Joannon et al. [105] investigated the classification of MILD combustion into separate regimes through experimentation and modeling of counter diffusion flames. Four zones were identified, namely, Homogeneous Charge Diffusion Ignition (HCDI) and auto-ignitive deflagrative regimes for high inlet temperatures, and ignition-assisted deflagrative regime and no combustion regimes at low inlet temperatures. Further classification was based on the degree of temperature rise of the inlet mixture, as sub-adiabatic and super-adiabatic regimes.

Derudi et al. [75] investigated the mild combustion of coke oven gas (CH4/H2 40/60 %) in a laboratory-scale burner. The transition to the flameless regime was marked by a sudden drop in NOx and CO levels [75]. Horizontal and vertical transition zones were
identified on a plot of inlet temperature and dilution ratio. An upper transition limit in temperature was determined that lead to excessive formation of NO\textsubscript{x}. They also found an upper limit in dilution ratio, beyond which poor combustion efficiency and high CO emissions resulted, due to a significant reduction in O\textsubscript{2} concentration.

Investigations on the acoustic oscillations in flameless combustion regime have also been undertaken [14, 111]. Lei et al. [111] investigated the effect of dilution of fuel with steam and observed a reduction in combustion oscillations and NO\textsubscript{x} due to reduction in flame temperature caused from dilution with steam. They also discussed that the liner wall temperature may increase with increasing steam dilution, possibly due to enhanced wall heat transfer. Joannon et al. [14] investigated the temperature oscillations during mild combustion of methane for a range of stoichiometries, inlet reactant temperatures and residence times. Modeling results were compared to experimental results in a spherical quartz jet-stirred reactor. The temperature oscillations were found to increase with decreasing residence time and dilution ratio, and were present for high enough reactor inlet temperatures in the range of 1000 to 1300 K, and C/O ratios higher than about 0.5. The competition between the CH\textsubscript{3} radical recombination reactions to C\textsubscript{2} species and oxidative routes has been associated with the oscillatory phenomenon. Adachi et al. [67] reported substantial reduction in combustion oscillations with multistaging.

Efforts on modeling combustors using a network of WSRs and PSRs have also been investigated [112, 113]. Many reactor network models have been proposed in the past, some of them applicable only to specific geometries [114–117]. The zonal concept was extended further to the development of detailed combustor reactor networks (CRNs) [118–121], with the view of bridging the gap between the simplistic modular approach that ignores fluid transport, and the computational fluid dynamics (CFD) approach, that fails to account for detailed reaction kinetics. However, in this work, we have used a simplistic continuously stirred tank reactor (CSTR) network model in order to avoid any uncertainties regarding estimation of flow-splits and in order to obtain fundamental and
sufficiently generic results, that may be applicable to any application or system (furnace, IC engine, gas turbine combustor, etc.).

Part of the current study has been to determine the blowout performance of various biofuels in the vitiated combustion regime. An early effort to study the vitiated combustion performance of conventional fuels was carried out by Harwood [44] using Recirculating Plug Flow Reactor (RPFR) and Perfectly-Stirred Reactor (PSR) models to characterize combustion efficiency and stability of combustors for SCC systems. Harwood’s work was an extension of the modeling effort of Crittenden [23] that was based on the approach of Strehlow [21]. These early efforts were primarily based on simplified global kinetic rates.

The modeling approach has been refined in this study, to include detailed chemical kinetics for the alternate fuels. While the present work primarily focused on predicting combustion performance, significant experimental work has been carried out by other researchers, over the years. The combustion stability for conventional open cycle engines using experimental Well-Stirred Reactors (WSRs) have been investigated by Longwell and Lang [106], Weiss et al. [107], Ballal et al. [108], Zelina and Ballal [109], Blust et al. [110], Stouffer et al. [122]. A simplified global reaction approach for Open Cycle (OC) engines has also been presented in Spalding [22].

2.2.5 Biofuel Vitiated Combustion

Ashen and Cushman [123] compared the combustion of biodiesel surrogate (methyl butanoate), ethanol and diesel fuel through experimentation as well as modeling of diesel engine. Biodiesel blends B0, B5 and B20 were used for comparison. The combustion behavior of B20 blend displayed a low temperature heat release (LTHR) cool flame, before the main combustion event [123]. The effect of EGR was studied by controlling the inlet temperatures [123]. It was found that, an intake temperature increase reduced ignition delay while increasing biodiesel percentage increased ignition delay, reduced unburned hydrocarbon (UHC) emissions (measured as equivalent CH₄ emissions), but increased
NO\textsubscript{x}. In addition, ethanol combustion produced significant CO\textsubscript{2} and CO emissions and no cool flame was observed, unlike the case of biodiesel.

Zheng et al. [66] investigated the combustion of B100 biodiesels derived from soy, canola and yellow grease in LTC using EGR on a diesel engine. They found that ultra-low NO\textsubscript{x} levels could be achieved by using very high EGR levels, and attributed the reduction to longer mixing times (due to increased ignition delays) and lower temperatures, resulting from vitiation. This tends to reduce overall NO\textsubscript{x}. Use of biofuels, had competing effects on ignition delays due to high cetane number (shortens delay) and high viscosity (lengthens delay) [66]. They found that soot was increased with EGR (high temperature combustion regime) initially, and then began to be reduced at very high levels EGR (low temperature combustion regime). It must be noted that the temperature of EGR stream has a significant impact on results too, however, is frequently not reported.

Agarwal et al. [124] suggested that the biodiesels produced lower particulate matter (PM) due to their lower aromatic content, higher oxygen content and short-chain paraffin hydrocarbons, in comparison to diesel fuel. They performed experiments on a diesel engine and found that NO\textsubscript{x} reduced with EGR and, the amount of reduction was higher at higher loads. They found 15 % EGR produced lowest NO\textsubscript{x} and that the smoke emission increased with EGR and load. The thermal efficiency increased with EGR at lower loads but remained unaffected at higher loads.

2.3 Combustion of Alternate Fuels

A brief background on the combustion performance of various biofuels has been presented in this section. Several inconsistencies have been observed in the results from different research efforts, for biofuel combustion.

2.3.1 Syngas

Previous studies on syngas have raised concerns over the compositional variability of syngas and its impact on turbine design. Syngas is also known to produce high NO\textsubscript{x} emissions at high H\textsubscript{2}/CO ratios, owing to potentially higher associated temperatures of
combustion, depending on the method of control. Inlet composition dilution, especially with N₂, is often resorted to limit the combustion temperatures to acceptable limits. Hence, operating syngas on a semiclosed cycle is of particular interest, since the EGR would result in lower overall combustion temperatures and lower NOₓ levels.

2.3.2 Biodiesel

Biodiesel fuel (BDF) consists of monoesters produced through transesterification of vegetable oils. The transesterification process involves conversion of triglycerides to glycerol and methyl ester upon reaction with methanol, in the presence of an acid or alkali catalyst. Alkali catalyses is faster and used commercially for transesterification [124, 125]. Biodiesel fuels have higher flash point and therefore are safer to handle [124]. However, biodiesel fuels have known issues with corrosion, fuel buildup and cold start problems. Bolszo et al. [126], Bolszo and McDonell [127] investigated the atomization, vaporization, combustion and emissions of biofuels. They found an increase in NOₓ and CO emissions resulting from poor atomization and vaporization characteristics of biodiesels, compared to diesel fuel. They have reported inconsistencies in literature regarding biofuel combustion performance [126]. They also suggested the use of ethanol/biodiesel blends to improve ignition characteristics, at the expense of heating value of the fuel.

Muncrief et al. [128] studied the effect of combining the use of biodiesel and EGR in IC engines. They concluded that a significant reduction in Particulate Matter (PM) and NOₓ was achievable. They reported that NOₓ emissions depended on the source of biodiesel and that highest NOₓ levels were obtained with the use of ultra-low sulfur diesel (ULSD), followed by soy-based B100 fuel, while cottenseed-based B100 fuel had lowest NOₓ levels. As suggested by references therein, NOₓ emissions were higher for fuels that were unsaturated to a higher degree, like canola or soy based biodiesel. They found an increase in PM with EGR, unlike what has been observed by Ellis et al. [12].

Metcalfe et al. [129] compared the combustion performance of two biodiesel surrogate fuels, frequently used for modeling biodiesel, namely ethyl propanoate (C₉H₁₈COOC₂H₅)
and methyl butanoate (CH$_3$CH$_2$CH$_2$COOCH$_3$), both with molecular formula C$_5$H$_{10}$O$_2$.

Shock tube experiments were performed for $\phi = 0.25-1.5$, temperature range of 1100-1670 K and at pressures of 1.0-4.0 atm., to study the ignition delay times of the fuels [129]. They found ethyl propanoate ignites faster than methyl butanoate.

2.3.3 Palm Methyl Ester (PME)

Hashimoto et al. [130] studied the combustion of palm methyl ester (PME) in gas turbine engine. PME is an important alternative fuel since, palm trees have high yield in comparison to other crops [130]. However, palm oil has a low pour point and hence needs heating of fuel lines to lower viscosity before fuel injection, in order to match that of diesel fuel used for comparison [130]. The sauter mean diameter (SMD) for PME was found to be slightly lower than that of diesel fuel, for the same injection pressure [130]. They suggested that the absence of aromatic content and the presence of oxygen content in the fuel resulted in lower soot formation in PME, in comparison to diesel fuel. The CO and total hydrocarbon (THC) emissions were found to be lower than 2 ppm (corrected to 16% O$_2$), for both fuels. NO$_x$ levels of PME were found to be lower than that of diesel fuel, and were found to increase with decreasing pressure of atomization, because of increase in SMD resulting in increased evaporation time and enhanced degree of diffusion-controlled envelope-combustion of droplets [130]. Local high temperatures at near stoichiometric conditions increase NO$_x$ levels. Hence, lower NO$_x$ of PME could be attributed to lower SMD of PME compared to diesel, for the same inlet kinematic viscosity [130].

2.3.4 Rapeseed Methyl Ether (RME)

Tsolakis et al. [131] investigated the performance of RME/diesel blends in compression ignition (CI) diesel engines with EGR. They found that an increase in the percentage of RME reduces smoke, UHC and CO emissions but increases NO$_x$ emissions. They found that RME had an effect of reducing ignition delay, increasing the fuel burning in the premixed phase, and consequently raising the pressure and temperature, and hence NO$_x$. It was less compressible, and hence the injection pressure was higher for RME blends,
increasing combustion pressure, temperature and NO\textsubscript{x} [131]. Soot reduction was achieved predominantly due to high oxygen content of fuel, since the oxygen content in the fuel-rich premixed reaction zones was increased. Additionally, RME has significantly lower sulphur content [131]. EGR had an effect of lowering the overall combustion temperature and increasing the ignition delay, thus reducing NO\textsubscript{x}.

Dagaut et al. [132] modeled the combustion of RME in a jet-stirred reactor and suggested n-hexadecane as a model fuel surrogate for RME. The modeling could not, however, capture the early CO\textsubscript{2} production, and over-predicted large olefins. The agreement between experiments and modeling was reasonably good otherwise.

Karabektas [133] studied the effect of RME biodiesel and turbocharging, on diesel engine performance. They attributed the improvement in brake thermal efficiency (BTE) of biodiesel to the oxygen content of the fuel, and its higher cetane number. Lower CO emissions of biodiesel were mainly an outcome of lower C/H ratio, higher oxygen content and higher cetane number (which result in lower ignition delays) [133]. NO\textsubscript{x} emissions were found to be higher and were attributed to the oxygen content of biodiesel.

2.3.5 Dimethyl Ether (DME)

DME has wide flammability limits and emission properties similar to those of natural gas [134]. It has low C/H ratio and has high oxygen content, is known to be non-toxic, has low auto-ignition temperature, high cetane number, higher volatility and has soot-free combustion [134]. However, it has drawbacks of having a lower lubricity, and decreased heating value due to its oxygen content [134].

Lee et al. [135] investigated the combustion of DME in a model combustor test facility. A comparison of combustion performance with respect to methane was presented. They found that DME presented lesser combustion instability, however, it had a tendency for flashback. They attributed the enhanced stability (lesser combustion oscillations) of DME compared to methane, to its greater molecular mass that shapes the flame lengthwise, and
to its lower heat release rate. The CO emissions for DME were much lower, while the NO\textsubscript{x} emissions were comparable to those of methane.

In their study, Sidhu et al. [25] found that DME was found to have an ignition delay a factor of three lower than that of compressed natural gas (CNG). Biodiesel, on the other hand, had a factor of two times larger ignition delay than diesel under similar conditions, despite its higher cetane rating [25]. They suggested that the higher viscosity of biodiesel resulted in larger biodiesel droplets, contributing to larger ignition delays.

2.3.6 Ethanol

Ashen and Cushman [123] reported in their study, that ethanol combustion produced predominantly CO\textsubscript{2} and CO emissions in the exhaust. The mechanism developed by Marinov [136] has been used to model the combustion of the fuel.

2.4 Soot Formation

2.4.1 Soot Structure, Properties and Health concerns

Soot particles consist largely of carbon atoms with about 1-3 \% hydrogen [137], and may contain other elements like oxygen [138]. The physical structure of soot consists of platelets grouped to form crystalites, which further group to form particles (5-50 nm) [137]. These particles then form clusters (0.6-0.8 microns) of fractal nature by agglomeration [137]. The spherules of soot (primary soot particles) in agglomerates (secondary soot particles) are of 10 to 80 nm size, although most particles fall between the size range of 15-50 nm [139]. There may be as many as 10\textsuperscript{5} to 10\textsuperscript{6} carbon atoms in a primary soot particle [139].

Soot is a commercial product used in copy machines and as an active filler in rubber products [9]. The radiation from soot particles is primarily responsible for flame spread in fires and contributes to combustion efficiency in furnaces [140]. The radiant soot particles in the flame tend to heat up the combustor liner and blades of the gas turbine [141–143]. The particulates from the combustion of certain fuels have been found to be linked to their high level of sulphur content [144].
The health and environmental effects of soot particulate matter have been extensively reviewed [144–147]. The particulate matter is generally classified as ultrafine particles (less than PM0.1), fine particles (less than PM1.0) and coarse particles (greater than PM1.0). The PM10 particles affect upper respiratory system, while the fine and ultrafine particles affect the lower respiratory system and may also enter alveoli, causing chronic respiratory disorders [144]. The polyaromatic hydrocarbon (PAH) molecules consisting of up to 16 carbon atoms (pyrene, A4) are precursors to soot formation. These have been hypothesized to dimerize and form the first soot nuclei [148–150] and then further grow through coagulation and surface growth. The carcinogenic character of the soot particulates has been attributed to the constituent PAH molecules as well as the adsorbed polycyclic organic matter (POM) [144].

Hopke [147] have discussed the changing trends in air pollution effected from changing global economic and political scenario’s. Further, they discussed the threat faced in over populated “megacities” like Dhaka, Beijing and Karachi. They presented air pollution data of several countries and compared it against the US regulatory standards. The regulatory standards of Environmental Protection Agency (EPA) [1] generally control particles of size PM10 and PM2.5. The US National Ambient Air Quality Standard (NAAQS) for PM2.5 is 15 $\mu g m^{-3}$ (annual average) and 35 $\mu g m^{-3}$ (24 hour average), while for PM10 is 150 $\mu g m^{-3}$ (24 hour average) [147]. The data from several countries was compared to these averages and it was found that a majority of these countries did not meet the US standard, even at the current pollution levels. With the shift of manufacturing industries from the west to east, the growth of the developing economies in the east would eventually be restricted by the need to meet the increasingly stringent pollution standards [147]. In another recent study, it was concluded that the PM have a significant greenhouse warming effect due to their long residence time and broad absorption spectrum, and that their reduction would have a huge impact on curbing the global warming problem in the short term [144, 147].
Dellinger et al. [146], in their summary of the 10th international congress on the health effects of combustion byproducts reported that, 70% of the aerosols in the atmosphere are released from combustion and 50% are primary pollutants from the sources of combustion. They suggested that combustion sources released significant nano-organic carbon (NOC), which are particles of sizes of the order of 2 nm, together with soot particles of sizes in the range of 20-50 nm. The NOC have been found to be hydrophilic, showing little tendency to coagulate and may be related to the toxicity of soot particles [146]. These NOC may be responsible for the oxidative stress, known to have adverse health effects [146]. Some of their health impacts include deposition in lower respiratory tract and alveoli, increased risk to lung cancer, reduced lung function in children, chronic obstructive pulmonary disease (COPD), arrhythmia, atherosclerosis, neurodegeneration of the central nervous system, etc. PM2.5 have been related to increased mortality rates, cardiovascular and respiratory dysfunction, COPD, asthma, pneumonia, etc [146]. Other reported PM related health effects include lung inflammation, irritation and may cause myocardial infraction, tachycardia, increased blood pressure and anaemia [145]. Most air pollutants including PM increase free radicals, normally generated in response to extraneous effects by the defense systems of organisms. This results in oxidative stress linked to several diseases like chronic inflammatory diseases, cataract, central nervous system (CNS) disorders, etc. In addition, these may also cause haemotological problems (CO, benzene) and cancer [145].

2.4.2 Factors Affecting Soot Formation

Soot formation is a complex phenomenon and depends on several combustion parameters such as fuel structure and type, pressure, temperature, equivalence ratio, EGR, etc. [137, 142, 143, 151–153]. The effect of fuel structure on soot formation has traditionally been quantified using experimental approaches and parameters such as smoke height, luminosity number (LN), Tesner sooting index (TSI)[154], diffusion flame blackness parameter (DFBP) [155].
The relative sooting tendency of fuel molecular structure has been extensively studied for premixed and diffusion flames ([a] Premixed flames: acetylene < alkenes < isoalkanes < n-alkanes < monocyclic aromatic hydrocarbons < naphthalenes. (b) Diffusion flames: paraffins < monoolefins < diolefins < acetylenes < benzenes < naphthalenes. [154]).

Amin et al. [156] performed CFD studies and investigated pressure effects on soot formation and NO\textsubscript{x}. They concluded that pressure had a significant effect on soot formation due to a reduction in oxidation from reduced OH concentrations at higher pressure, as well as higher associated temperatures. Further, it has been found that pressure has a tendency of shifting the soot-bell maximum towards higher temperatures [157]. This effect was found to be stronger at lower pressures. Frenklach et al. [157] explained this phenomenon as resulting from the pressure-dependent unimolecular fragmentation route (slow route) of PAH, that competes with the condensation of PAH into Peri-Condensed Aromatic Hydrocarbons (PCAH) and subsequently soot (fast route).

The applicability of the model developed by Frenklach and Wang [149] was extended to high pressure flames by Kazakov et al. [158]. It was found that pressure had a tendency to increase acetylene concentration, and therefore, surface growth. Brown et al. [159] modeled the effect of pressure on combustion of ethylene fuel in a PSR. They found a shift in the peak of the soot-bell towards higher temperatures, accompanied by higher soot volume fractions at higher pressures.

Swirl also has an effect on soot formation, and has been found to decrease the sooting levels [160]. The formation of soot typically has a bell-shaped temperature dependency and forms at equivalence ratios greater than about two (critical equivalence ratios are in the range of 1.8 to 2.1) and temperatures between 1600 and 2600 K [141]. The critical soot inception temperature is about 1600 K and is known to be independent of fuel type [78].

Warnatz et al. [161] have shown the trend of increasing soot formation with decreasing hydrogen content in the fuel. The soot formation increases with pressure, C/H ratio, C/O
ratio, while displaying bell-shaped temperature dependence. This bell shaped dependency is due to the absence of pyrolytic radical products at lower temperatures and increased oxidation at higher temperatures, bounding the soot formation process to within 1000 to 2000 K [161]. The temperature range for soot formation according to Wagner [162] is around 1300 to 2800 K.

For pressure atomizers the main zone for soot formation is the oxygen deficient fuel spray zone [142]. The soot emission levels can be reduced by allowing more time, temperature and turbulence (three T’s) in a combustor [161], which on the other hand results in higher thermal NO production. Therefore, the simultaneous optimization particulate carbon, CO, UHC and NO$_x$ emissions can be challenging.

The effect of equivalence ratio has also been investigated [163]. The odd carbon atom and aromatic species exhibit larger sensitivity to equivalence ratios, in comparison to the aliphatic molecules [163]. Moreover, the soot sensitivity to equivalence ratio was comparable to that of benzene [163]. The onset of soot inception occurs at an equivalence ratio of about 2, corresponding to C/O of 0.5 [161, 162]. The incipient particles are thought to be of the size range between 300 to 1000 amu and have an effective diameter of about 1.5 nm [139]. Wagner [162] has presented the data for soot inception C/O ratios for various experimental configurations, including bunsen flames, stirred reactors and flat flames. Based on their global reaction (as given below), the critical equivalence ratios may be obtained using equation 2–1 and equation 2–2.

$$C_xH_y + \alpha (O_2 + 3.76N_2) \rightarrow 2\alpha CO + \frac{y}{2}H_2 + (x - 2\alpha) C + 3.76\alpha N_2$$

$$\alpha = \frac{\alpha_{stoich}}{\phi} = \frac{1}{\phi} \left( x + \frac{y}{4} \right)$$

Therefore,
\[ \phi = \frac{1}{\alpha} \left( x + \frac{y}{4} \right) = \frac{2C/O}{x} \left( x + \frac{y}{4} \right) \] (2-2)

Hence for C\(_2\)H\(_4\), with critical \( \alpha = 0.60 \) [162], \( \phi = 1.80 \). Increasing temperature increases the threshold value of the equivalence ratio for soot formation [162]. A key challenge in soot modeling is the fact that the observation of the PAH species is limited to sizes less than 300 amu (using gas chromatography), while the smallest observable soot particle sizes are of the order of 1.5 nm [139]. In diffusion flames, the effect of dilution of fuel or air streams is that of reduction in the sooting tendency [162]. The review article by Mansurov [9] discussed the presence of two thresholds for soot formation at different temperatures for various fuel-air flames at different pressures.

### 2.4.3 Soot Formation Studies

Macadam [98], Kowalik et al. [101], Stouffer et al. [122], Brown et al. [159], Manzello et al. [164] have studied soot formation in WSRs. Modeling of soot in WSR/PSR/PFR or other configurations (both models and experiments) have been performed by [58, 77, 101, 122, 141, 159, 164]. Other studies on soot formation and soot include those of [102, 103, 139, 156, 165–169]. Similar zero-dimensional detailed chemical kinetic studies have been applied for flameless combustion, to predict flame stability [14, 58], and emissions [77, 87, 88].

Colket III et al. [141] modeled the soot formation process in a WSR for ethylene and ethylene-ethanol mixtures. They also discussed the effect of heat loss and the soot bell, in their comparison of the experimental data with the model. They concluded that the addition of ethanol had an effect of increasing soot, due to lowering of the flame temperature (on high temperature side of the soot bell).

Song and Zhong [166] modeled soot formation in diesel engine combustion using CFD modeling. They used the reduced mechanism of n-heptane pyrolysis and soot formation, combined with the method of moments to predict soot particle size distribution. The overall stoichiometry was fuel-lean, and they found that the oxidation rates were much
larger than the soot growth rates, resulting in short lifetimes of the soot particles. The PAH formation rates were very low. The model was found to underpredict the PAH concentrations and soot number density.

Brundish et al. [167] measured the soot particle size distribution in a combustor using scanning mobility particle sizing (SMPS). They used a smoke meter and an optical nephelometer for soot mass measurements, and an SMPS to obtain soot particle size distribution and soot volume fraction data. The soot number densities were found to vary between 4.4e7 to 1.08e6 and the particle sizes varied between 60 to 200 nm. A comparison of the results from SMPS and soot mass measurements provided an estimation for soot density. They obtained a density estimate of 132 to 3025 kg/m$^3$ as compared to values of 1500 kg/m$^3$ and 1850 kg/m$^3$ proposed by other researchers. The Frenklach particle growth model uses a value of 1800 kg/m$^3$ [149].

Manzello et al. [164] measured sooting levels in a WSR/PFR setup, using differential mobility analyzer (DMA), ultrafine condensation particle counter (UCPC) and transmission electron microscopy (TEM). The temperature in the WSR was controlled by adding inerts (N$_2$) to the WSR. Higher N$_2$ flow suppressed the peak soot number density and reduced the average particle diameters from 10 nm to about 3 nm in the temperature range of 1723-1558 K. They found a critical soot inception temperature of about 1558 K.

Stouffer et al. [122], Colket et al. [170] studied the effect of fuel additives on an nheptane/toluene flame in a WSR. The fuel additive compounds nitromethane, nitroethane, nitropropane, cyclohexanoane, pyridine and quinoline were tested. Pyridine and quinoline reduced soot through reduction of acetylene concentration while the other additives were oxydizing type, and reduced soot by virtue of their oxygen content. The effect of soot bell was also discussed. They found quinoline to be a poor additive, while nitroalkanes, although effective in reducing soot, increased NO$_x$. Cyclohexanone was found to reduce soot over all tested equivalence ratios, and had no impact on NO$_x$ levels. The authors also emphasized that the effect of additives was system dependent.
Frenklach et al. [171] modeled the detailed soot formation chemistry and particle growth and oxidation using the method of moments. Shock tube pyrolysis study was conducted on the fuels 1,3-butadiene, benzene and ethene, in order to characterize fuel effects on soot formation. They found that fuel structure affected soot formation through generation of intermediates that may participate in the chemistry to form PAH molecules and, by affecting generation of H atoms. The modeling of aromatic and aliphatic fuels revealed significant interaction of aromatic ring with acetylene. Results from alcohol-benzene mixture combustion revealed reduction of soot formation probably due to reduction of H atoms and increase in C₂H₂.

Kronholm and Howard [168] studied the particle growth process in PFR at equivalence ratio of 2.2, flame temperatures of 1520 and 1620 K, at a pressure of 1 atm. They found oscillatory behavior of the surface growth rate constant and proposed that such variation could be reconciled by assuming PAH to be the predominant growth species. They also rejected the possibility of sharp decline in apparent C₂H₂-soot reactivity on reduction in H concentrations as proposed by other researchers.

Brown et al. [159] modeled soot formation of ethylene-Ar flame in a PSR using CHEMKIN III. They predicted the variation sooting characteristics with equivalence ratio, temperature and pressure. They found that with increasing pressure the degree of coupling of the gas-phase and surface chemistry increased.

Balthasar et al. [165] modeled the effect of finite mixing rates on soot formation using PaSPFR model. Tuovinen [169] studied CO formation from soot and soot particle growth in hot gas layer using PSR model in Chemkin. The simulations were run for equivalence ratios 0.5-4.0 and residence times of 0.25-10 s. It was found that the reaction of soot and CO₂ increased CO generation and reduced soot volume fraction.

2.4.4 Soot Formation Models

There has been significant progress in the field of soot formation over the past few decades. Several review papers [9, 138, 172–177] have summarized the most critical work
in this area. Several empirical and semi-empirical approaches to modeling soot formation have been applied in the past [137, 142, 143, 152, 153]. Soot has also been modeled using CFD studies and phenomenological models in the works of [88, 156, 160, 166]. Phenomenologically, soot formation involves particle inception, surface growth, coagulation and aggregation processes [161].

Several soot formation models have been proposed in the past. Some of the names given include atomic carbon theory, C$_2$ theory, C$_3$ theory, acetylene theory, polymerization theory, Boudouard reaction theory, polyacetylene theory, polyaromatics, etc. [9, 138]. Proposed intermediates in the soot formation process include, ions, PAH, polyacetylenic chains ((C$_2$H$_2$)$_n$), polyenes, fullerenes, and neutral radicals [178]. Polyacetylene theory has the drawback that the rearrangement of polyacetylenes to aromatic ring structures would have a much longer timescale [138]. A mechanism based on polyene polymerization reactions has been proposed by Krestinin [179]. Some of the detailed models for soot formation proposed include those by Calcote [138], Frenklach and coworkers [148–150] and, Howard and coworkers [180–184]. The soot aerosol dynamics have been modeled using sectioning approach [180, 185, 186] and the method of moments [149, 187–189].

Higher aromatic chains upto C$_{60}$ have been modeled by Richter mechanism [180–183]. The closed ring aromatic structures are more stable and abundant in soot particles, and are known as Fullerenes [9]. The open chain ring aromatic structures, on the other hand are not stable. Fullerene molecular species C$_{60}$, C$_{70}$ and heavier fullerenes upto C$_{116}$ have been identified in flames [9]. Amorphous carbon, through internal redistribution of solid-state carbon, particle deposition and gas phase reactions, transitions into an ordered Fullerene structure [9]. The Corannulene subsystem has been found in almost all fullerenes, and thought be the precursor to Fullerenes [9]. The hydrogen abstraction acetylene addition (HACA) mechanism with corannulene has been proposed as the growth mechanism for fullerenes [9]. Richter et al. [180–183] have modeled the detailed chemistry of soot formation through reactions of PAHs.
The model proposed by Calcote [138] was based on ionic interactions and is no longer employed in studies. Calcote [138] in their critical review on soot formation process presented several supporting evidences for soot formation to be resulting from ionic mechanisms. They suggested that ions were present in significant concentrations in flames to serve as precursors for soot formation. Calcote [138] reviewed the effect of electric fields, chemical additives, electron addition, etc. on soot formation and cited pertinent literature that discussed role of ionic mechanisms in soot formation. For example, experimental work has shown that the concentration of positively charged particles peaks before the soot inception in a burner flame. Electric fields may be used to control soot growth by controlling the residence time of the charged soot particles within the flame zone [138]. It has also been shown that thermal ionization cannot account for the presence of large molecular weight ions in flames [138].

The soot formation process in this study, has been modeled using detailed chemical kinetic mechanism for soot formation by Frenklach and coworkers [148]. The soot formation model formulated by Frenklach and coworkers [148–150], is a multi-step process starting with gas phase kinetics.

Briefly, the soot growth mechanism in gas phase may proceed through either a low temperature route or a high temperature route [149]. The aliphatic molecules undergo dehydrogenation and sequential polymerization (HACA reactions, propargyl combinations, etc) resulting in formation of unsaturated hydrocarbons, cyclical molecules and eventually aromatic molecules [157]. Further growth of aromatic molecules may occur through ring-ring condensation reactions (formation of biphenyl [148]) or HACA mechanism. The ring-ring condensation reactions are known to quickly equilibrate and bulk of the aromatic growth proceeds through acetylene addition route [149]. The growth of aromatic molecules beyond a critical size eventually leads to nucleation/inception of three-dimensional soot particles, further modeled by a particle growth and oxidation model. These particles are large enough to be held together by Van-der-waals forces [161]. These soot particles
further undergo coagulation and aggregation, resulting in particle growth. Simultaneously, the particles may oxidize or polymerize at the surface resulting in reduction or growth of particle size and mass. The entire process has been modeled using the moments approach [187, 188, 190], to characterize the particle size distribution. The soot number densities, soot volume fraction and even optical properties may be estimated through this model. Xi and Zhong [139] also discussed the carbonization of mature soot particles that results in a transition of amorphous soot particles to a more graphitic structure. The future models for soot formation, may also be able to predict the particle morphology in addition to the other observables.

Several mechanisms have been proposed to characterize the soot growth process. Substantial mass addition occurs through the soot growth process without affecting the number density [139]. On the other hand, the particle coagulation process increases the soot volume fraction and decreases the number density, without affecting the total mass [139]. Mauss et al. [191] proposed a modified HACA scheme for surface growth that also accounted for the reduction of surface growth at high temperatures. In their modeling of laminar premixed flames, they showed that the decrease of radicals with decreasing flame temperature resulted in reduced soot formation rates. They concluded that the HACA mechanism was capable of describing the decay of soot growth rate, as interpreted from the phenomenological model, accurately.

Details about the detailed kinetics and particulate growth and oxidation models may be found in the work of Frenklach and coworkers [148–150, 158, 171, 187–190, 192–201]. The Frenklach chemical kinetic mechanism consists of aromatic molecules up to four benzene ring structures: benzene (A₁), naphthalene (A₂), acenaphthene (A₃) and pyrene (A₄). Some of the important intermediate PAH molecules include naphthalene, acenaphthalene, phenanthrene, pyrene and coronene [138].
2.4.5 Soot Formation Chemistry

The chemical mechanism of soot formation proposed by Appel et al. \cite{148} includes initiation reactions, pyrolysis reactions, reactions for formation of first aromatic ring, and aromatic growth and oxidation via HACA \cite{148}. The mechanism is based on acetylene (even-carbon) channels, in contrast to the mechanism (based on odd-carbon chemistry) proposed by Marinov et al. \cite{148}.

Wang and Frenklach \cite{195} presented a detailed chemical kinetic model (99 species, 527 reactions) for PAH formation in acetylene and ethylene flames. The reactions of lighter species (C$_1$/C$_2$ Species, H/O reactions) was taken from GRI-Mech 1.2. They also added reactions to account for aromatic ring formation through the propargyl channel, the formation of which occurred by reactions of C$_1$ and C$_2$ molecules \cite{195}. The 1,3-butadiene (1,3-C$_4$H$_6$) and vinyl acetylene (C$_4$H$_4$) formation reactions proceed through reactions of two C$_2$ species (vinyl, acetylene, etc.) or via reactions of C$_1$ and C$_3$ radicals \cite{195}. The rate coefficient for the abstraction of 1,3-C$_4$H$_6$ was estimated, since experimental data wasn’t available.

\[ \text{C}_2\text{H}_3 + \text{C}_2\text{H}_2 \rightleftharpoons \text{C}_4\text{H}_4 + \text{H} \]

\[ \text{C}_3\text{H}_3 + \text{CH}_2 \rightleftharpoons \text{C}_4\text{H}_4 + \text{H} \]

\[ \text{C}_2\text{H}_4 + \text{C}_2\text{H}_3 \rightleftharpoons 1,3 - \text{C}_4\text{H}_6 + \text{H} \]

\[ \text{C}_3\text{H}_3 + \text{CH}_3 \rightleftharpoons 1,2 - \text{C}_4\text{H}_6 \]

\[ 1,2 - \text{C}_4\text{H}_6 + \text{H} \rightleftharpoons 1,3 - \text{C}_4\text{H}_6 + \text{H} \]

Formation of the benzene ring, proceeded through the following dominant routes:
\[ n - C_4H_3 + C_2H_2 \rightarrow n - C_6H_5 \rightarrow \text{phenyl} \]

\[ n - C_4H_5 + C_2H_2 \rightarrow n - C_6H_7 \rightarrow \text{benzene} + H \]

Additional routes from \( n\)-\(C_4H_5\), \( n\)-\(C_4H_3\) (and resonantly stabilized isomers i-\(C_4H_3\) and i-\(C_4H_5\)) and propargyl (\(C_3H_3\)) radicals were also included [195]. These reactions result in the formation of non-aromatic \(C_6H_6\) adduct that eventually isomerizes to benzene, through internal rearrangements. In comparison, the \(C_3H_3\) reactions require less intermediate steps to form benzene, and hence are of higher significance. However, Wang and Frenklach [195] did highlight the possibility of intermediate steps such as the formation of non-aromatic \(C_6H_6\) adduct with propargyl route also, thereby treating the propargyl radicals only as global steps. They also concluded that the production of aromatics through the \(C_4H_3\) and \(C_4H_5\) channels could be comparable to that from the \(C_3H_2\) channel, depending on the flame conditions.

\[ n - C_4H_3 + H \Leftrightarrow i - C_4H_3 + H \]

\[ n - C_4H_5 + C_2H_2 \Leftrightarrow i - C_4H_5 + H \]

\[ C_3H_3 + C_3H_3 \Leftrightarrow \text{benzene} \]

\[ C_3H_3 + C_3H_3 \Leftrightarrow \text{phenyl} + H \]

Further, they highlighted the uncertainties in the oxidation reactions of phenyl/PAH. The PAH growth process followed the HACA mechanism [195]. Reactions with ethynyl radical (\(C_2H\)), and the oxidation channels of OH, O and \(O_2\) were also added. Comparison
with experimental results indicated underprediction of H and CO, an overprediction of OH, while the important intermediates were predicted well. The PAH formation and growth reactions have been found to be highly reversible, with the formation of stable intermediates like pyrene and acenaphthalene proceeding through nearly irreversible reactions [148]. The reversibility of the reaction steps, has the effect of building a thermodynamic barrier, while the irreversible steps help the reaction progress forward [148].

Richter and Howard [182, 202] have discussed the importance of PAH formation routes through the recombination of propargyl (C₃H₃) and cyclopentadienyl (C₅H₅) radicals. It has also been shown that HACA mechanism alone, may not be adequate for prediction of the rates of formation of some of the PAH molecules [181].

The propargyl recombination route is the most dominant pathway to formation of benzene [148]. Appel et al. [148] also added the reaction step for addition of vinyl acetylene to aromatic radicals. Formation of naphthalene (A₂) proceeds predominantly through this route, while phenanthrene (A₃) generation mostly follows the ring-ring condensation route (formation of biphenyl) [148].

2.4.6 Soot Nucleation

The soot nucleation phenomenon is not well understood. Several chemical species have been proposed as potential soot precursors. Soot inception is believed to start at molecular weights of 500 to 2000 amu (approx. C₄₀ or larger molecules) [161]. Schuetz and Frenklach [203] presented convincing arguments about the possibility of pyrene molecules being precursors to soot nucleation. In their computational studies, they found that dimerization of pyrene resulted in stable intermediates that may be considered as soot nuclei. Glassman et al. [78] found that soot inception began around 1600 K and that the inception temperature was independent of the fuel. Manzello et al. [164] found a critical soot inception temperature of about 1558 K in their WSR experiments. Frenklach and Wang [150] modeled the nucleation process using method of linear lumping of an infinite
HACA reaction set. Frenklach [190] assumed that the first molecule in the polymerization block had 24 carbon atoms.

Miller et al. [178] showed that dimer concentrations are typically low, in order for these to produce requisite number of nucleation sites. However, their study was based on estimation of equilibrium constants, to which Frenklach [150] argued that low dimer concentrations could still be justified since, the PAH polymerization process is predominantly governed by chemical kinetics, and may still proceed through formation of quasi-steady state stable dimer intermediates through irreversible reactions in a chemical kinetic sequence.

Dobbins and Subramaniasivam [204] observed singular polydisperse incipient soot microparticles (upto 15 nm) in laminar premixed flames using TEM. These were found to be more mature soot particles; different from the incipient PAH molecules proposed by other researchers. They suggested that these incipient particles undergo dehydrogenation (annealing) at the high temperature flame front, to form graphitic soot particles. They hypothesized that these nearly transparent particles to electron beam, were predominantly made up of PAH fragments, and that a (liquid-like) coagulation process resulted in their subsequent growth.

Glassman et al. [78] performed experiments on critical sooting temperatures by controlling soot inception by dilution with $N_2$. They found the threshold to be around 1600 K irrespective of fuel type and diluent used. They also discussed that the oxidation rates are nearly zero below 1300 K, and therefore suggested an oxidative regime between 1300-1600 K for as a soot reduction strategy.

2.4.7 Soot Growth and Oxidation

Over 75% of soot mass addition results from soot surface chemistry [9, 161]. The particle size is, therefore, a strong function of equivalence ratio, unlike the particle number density [162]. However, frequently this process is modeled using phenomenological
approach equation 2–3. Other more detailed models for soot particle growth have also been proposed [205].

\[
\frac{df_v}{dt} = k_{sg} (f_v^\infty - f_v)
\]  

(2–3)

Appel et al. [148] presented revised submodels for gas phase chemistry, coagulation and surface growth (to accurately model the decay of surface reactivity) and validated the models against experimental results for C\textsubscript{2} hydrocarbons. The model was adapted from a previously developed model of Wang and Frenklach [195].

Soot oxidation results in reduction of soot size through reaction with oxidizers OH and O\textsubscript{2}. The concentration of O radicals is very low, and hence is not considered as a key oxidizing species. The process of soot oxidation, may occur simultaneously as in premixed systems (WSRs, premixed flames, etc.), or in a subsequent process as in diffusion flames [139]. Several oxidation models have been proposed [139], including those by Marsh and Kuo, Neoh et al. [206] and Nagle and Strickland-Constable.

Neoh et al. [206] suggested that the oxidation model of Nagle and Strickland-Constable may not be able to correctly predict oxidation due additional oxidizers (OH, O, etc.), besides O\textsubscript{2}. In their predictions, the soot oxidation rate was overestimated when the oxidation by OH, in fuel-rich conditions, was neglected. Neoh et al. [206] studied the burnout of soot-laden gases in an oxidative environment of a secondary flame. In their experiments, the flame environment was controlled by varying the amounts of N\textsubscript{2}/CO\textsubscript{2}/CH\textsubscript{4}/O\textsubscript{2} gases injected into the system. The collision efficiencies (ratio of the experimental reaction rates to those determined from collision theory) were calculated for OH, O\textsubscript{2}, O, CO\textsubscript{2}, H\textsubscript{2}O. They discussed the relative oxidative effects of O\textsubscript{2}, OH and O and suggested that OH was the dominant oxidizer in fuel-rich conditions while O\textsubscript{2} being a significant contributer in fuel-lean conditions. The significance of O was found to be only secondary in fuel-rich conditions.
CHAPTER 3
DESCRIPTION OF MODEL

3.1 Soot Formation Model

Currently, one of the most widely accepted models of soot formation is the detailed soot formation model proposed by Frenklach and coworkers [149], and a summary of their model has been described in this section. The model includes a detailed chemical kinetic mechanism for gas phase chemistry of soot formation. The gas phase chemistry also includes the polyaromatic hydrocarbons (PAH) molecule growth up to 4 aromatic ring pyrene (A4) molecule. To model planar PAH and subsequent 3-dimensional soot particulate growth, a coupled aerosol dynamics model was proposed. This model includes submodels for PAH planar growth chemistry simplified by chemical lumping techniques [190, 207], particle nucleation [150], PAH condensation, surface growth and oxidation using simplified hydrogen-abstraction-acetylene-addition (HACA) mechanism, particle coagulation, and particle aggregation. These submodels were coupled into a method of moments [187–189], that utilizes sectioning approach, common to aerosol models. The figure 3-1 outlines the basic processes of soot formation.

Figure 3-1. Soot Formation - Particulate Model
In summary, the detailed soot formation model may be broadly categorized into the following submodels:

1. detailed gas-phase kinetics
2. planar growth of PAH
3. particle nucleation
4. particle coagulation
5. particle aggregation (neglected)
6. surface growth and oxidation- PAH condensation, HACA chemistry

3.1.1 Method of Moments

This method [149, 187–189, 208] allows characterizing the particle distribution functions using smaller number of equations to solve for its moments. The method of moments with interpolative closure (MOMIC) described in Frenklach [187] has been developed from the Method II for polydisperse distributions, described in Frenklach and Harris [188]. The $r^{th}$ moment of a distribution with $N_i$ particles with size $m_i$, may be written as equation 3–1. Further, the size moments $\mu_r$ may be calculated by normalizing
the concentrations moments $M_r$ (normalized to $M_0$). The particulate soot model calculates the average soot diameter, soot volume fraction, soot surface area, from calculation of moments of the soot particle distribution, determined by summing up the contributions of moments, as given by equation 3–2 from each of the submodels.

$$M_r = \sum_{i} m_i^r N_i \quad (3–1)$$

$$\frac{dM_0}{dt} = R_0 - G_0 + W_0 \quad (3–2)$$
$$\frac{dM_1}{dt} = R_1 + G_1 + W_1$$
$$\frac{dM_r}{dt} = R_r + G_r + W_r$$

where $R_r$, $G_r$ and $W_r$ are the moment rates of formation due to nucleation, coagulation and surface growth respectively. The basic assumption is that the rates of all the three processes are additive [187]. The individual rates of each of these processes has been derived in subsequent sections. The rate $W_0$ is assumed to be zero, since the surface chemistry is not expected to affect the number densities. On the other hand, the coagulative first moment production rate $G_1$, is treated as zero. The possible explanation being that, if a control volume is drawn around the soot particles, the coagulative processes, would operate only within the control volume, no net mass transfer occurs across the control volume. In other words coagulation would only redistribute the number densities within the existing size classes, but no additional mass transfer will occur across the boundary between the particles and the gas mixture.

The consumption of gas phase species in the growth and oxidation of soot particles is accounted for by correcting the production terms of the gas phase species. The moments are integrated, together with other state variables of the reactor. The conservation equations for species and moment balances are given by equations 3–3 and 3–4, respectively.
The correction term for species production rate, as given by equation 3–5 needs to be applied, in order to account for the species consumption in particulate chemistry.

\[
\left( \frac{dm_j}{dt} \right)_{CV} = (\dot{m}_{in}y_{j,in} - \dot{m}_{ex}y_{j,ex}) + (\bar{M}_jV_R\dot{\omega}_j) \tag{3-3}
\]

\[
\left( \frac{dM_r}{dt} \right)_{CV} = \frac{1}{V_R} \left( \frac{\dot{m}_{in}M_{r,in}}{\rho_{in}} - \frac{\dot{m}_{ex}M_{r,ex}}{\rho_{ex}} \right) + (\dot{Q}_r) \tag{3-4}
\]

\(\dot{Q}_r\) is the formation rate \((cm^{-3}s^{-1})\) of the \(r\)th moment \(M_r\) \((cm^{-3})\). If the array size of species production rates \(\dot{\omega}_j\) is modified to include the moment formation rates, and the species production rates are corrected for soot production, the resulting system of equations \([208]\), is given by equation 3–5 through equation 3–8.

\[
\dot{\omega}_j' = \dot{\omega}_j + \dot{\omega}_j^{corr}; j = 1, ..., n_j \tag{3-5}
\]

\[
\omega_{j+r+1}' = \dot{Q}_r; r = 0, ..., n_r - 1
\] \tag{3-6}

\[
\left( \frac{dm_j}{dt} \right)_{CV} = (\dot{m}_{in}y_{j,in} - \dot{m}_{ex}y_{j,ex}) + (\bar{M}_jV_R\dot{\omega}_j'); j = 0, ..., n_j \tag{3-7}
\]

\[
\left( \frac{dM_l}{dt} \right)_{CV} = \frac{1}{V_R} (\dot{m}_{in}M_{l,in} - \dot{m}_{ex}M_{l,ex}) + (\dot{Q}_l); l = (n_j + 1), .., n_j + n_r \tag{3-8}
\]

Hence, the output of soot particle growth model yields the moment production rates \((\dot{Q}_r)\) and the species correction terms \((\dot{\omega}_j^{corr})\) for species A4, C2H2, CO, H, H2, H2O, O2 and OH. These were obtained from the soot particulate code \([208]\). The species conservation equations in the Cantera continuously stirred tank reactor (CSTR) code, had to be modified to couple the solution of the soot moments at each time step. A derived class was written in C++, that modified the functionality of the Reactor class in the original Cantera distribution. This class allowed the modified conservation equations
to be solved by coupling the moment production and species correction terms obtained from simultaneous solution of the fortran soot code [208], using extern commands. A less accurate approach [158] sometimes used in the past is to solve soot moments decoupled from the CSTR/PSR solution.

3.1.2 Gas Phase Kinetics

The gas phase chemistry of soot formation has been described in Appel et al. [148], Frenklach and Wang [149], Wang and Frenklach [195], Frenklach [197], and has been adapted from a GRI-Mech 1.2, for fuel pyrolysis reactions. Appel et al. [148] proposed a new chemical kinetic mechanism with modifications to that of Wang and Frenklach [195]. The starting point of formation of the first aromatic ring is vinyl addition to acetylene through formation of n-C$_4$H$_5$, in case of low temperature reactions or n-C$_4$H$_3$ in case of high temperature reactions. Another route to formation of benzene ring, is the combination of propargyl radicals (C$_3$H$_3$) [149]. The formation of higher PAH molecules proceeds through the *hydrogen abstraction and acetylene addition (HACA reactions)*. For aromatic fuels, the cyclization reactions of the aromatic rings become predominant. Such systems, however, relax back to the HACA mechanism, once the acetylene concentration increases to a critical value [149]. In the earlier version of the soot models, the species A$_6$-A$_8$ were treated using chemical lumping while particulate soot was defined as cumulative aromatic content beyond benzo[ghi]pyrene (A$_6$) [193]. In the model described in [149], the PAH growth beyond acepyrene was modeled using chemical lumping. Subsequent nucleation process was modeled as resulting from the coalescence of these PAH molecules [149]. The collisions lead to dimeration of the PAH molecules, causing particulate nucleation. In current version of the model, nucleation was treated as resulting from dimerization of two pyrene molecules [208]. There is no explicit treatment for PAH planar growth beyond pyrene, while growth upto pyrene is included in gas phase chemistry submodel. However, the moment contributions from the reduced HACA mechanism for surface growth may be derived through the chemical lumping technique.
3.1.3 PAH Planar Growth

The PAH molecules undergo infinite set of cyclization reactions and grow in size. This infinite reaction mechanism is modeled using a finite reaction set, using method of linear lumping that yields moment rates due to planar growth of PAH. Frenklach and coworkers [149, 189, 207] proposed an HACA mechanism of lumped PAH species, to model the infinite PAH growth. Subsequently, a reduced HACA mechanism was utilized for modeling surface chemistry by a few HACA reactions, as well as oxidation with O$_2$ and OH species [148, 158]. A differential equation set for moment rates of the PAH distribution function, may be used to characterize profiles from the PAH polymerization reactions. The $r^{th}$ concentration moment is given by equation 3–9 while the size moment is given by equation 3–10.

\[ M_r^{PAH} = \sum_{i=i_0}^{\infty} m_i^r N_i^{PAH} \]  

(3–9)

\[ \mu_r^{PAH} = \frac{M_r^{PAH}}{M_0^{PAH}} \]  

(3–10)

where $m_i$ gives the number of carbon atoms in the size class $i$. It is assumed that only C atoms contribute to the mass of a particle, while that from H atoms is neglected.

The general scheme of linearly lumping a sequential reaction mechanism has been shown in figure 3-3. It also shows how the HACA reaction mechanism described in [149] may be reduced to a sequential reaction set, assuming all reactions are first order and depend only on the concentrations of polymerizing aromatic hydrocarbons. The rate constants however, may be functions of the concentrations of non-polymerizing gas-phase species.

For example, consider reaction $L_2$ in the reaction block described in [149], given by $A_i \ast + C_2H_2 \rightleftharpoons A_iC_2H + H$. This reaction may be considered to be a first order reaction $A_i \ast \rightleftharpoons A_iC_2H$ with rate constant $k_{L2} = k_{L2}(A, E, n)[C_2H_2]$ and $k_{-L2} = k_{-L2}(A, E, n)[H]$. 

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Let $i, j$ be the block (or reaction class) and species index-variables, respectively, while $r$ and $s$ be the indices of reactions and species in each block. The total number of reactions in a block is $n_r$ and total number of species in a block is $n_s$. Let $S_j$ represent all possible reacting species of size class $j$ while $S_{is}$ represent species $s$ in block $i$. Hence, $S_{is} = S_{s+(i-1)n_s}$. The goal is to estimate the rate of production of individual species in the infinite sequence by information in one replicating block, by breaking down the reaction sequence into identical finite number of reaction classes [149]. Consider, the production rates of all PAH beyond the incipient species $A_{i0}$, which may be calculated using equations 3–11 through 3–15. The rate of formation of the incipient species ($k_0$) is calculated from the gas phase species productions rates of soot precursors, available from kinetics-coupled CSTR solution.

$$\frac{d[S_1]}{dt} = k_0 - k_1[S_1] + k_{-1}[S_2]$$  \hspace{1cm} (3-11)$$

$$\frac{d[S_2]}{dt} = k_1[S_1] - (k_{-1} + k_2)[S_2] + k_{-2}[S_3]$$  \hspace{1cm} (3-12)$$
\[
\frac{d[S_3]}{dt} = k_2[S_2] - (k_{-2} + k_3)[S_3] + k_{-3}[S_4]
\] (3–13)

\[
\frac{d[S_4]}{dt} = k_3[S_3] - (k_{-3} + k_4)[S_4] + k_{-5}[S_5]
\] (3–14)

Generalizing for \( j > 1 \),

\[
\frac{d[S_j]}{dt} = k_{(j-1)}[S_{(j-1)}] - (k_{-(j-1)} + k_j)[S_j] + k_{-j}[S_{(j+1)}]
\] (3–15)

\[
K = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & \ldots & \ldots \\
k_0 & -k_1 & k_{-1} & 0 & 0 & 0 & \ldots & \ldots \\
0 & k_1 & -(k_{-1} + k_2) & k_{-2} & 0 & 0 & \ldots & \ldots \\
0 & 0 & 0 & 0 & 0 & 0 & \ldots & \ldots \\
0 & 0 & 0 & 0 & 0 & 0 & \ldots & \ldots \\
0 & 0 & 0 & 0 & k_{j-1} & -(k_{-(j-1)} + k_j) & k_{-j} & \ldots \\
0 & 0 & 0 & 0 & 0 & 0 & \ldots & \ldots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots
\end{pmatrix}
\]

\[
S = \begin{pmatrix}
1 \\
S_1 \\
S_2 \\
S_3 \\
S_4 \\
S_5 \\
S_j \\
\vdots
\end{pmatrix}
\]
Hence the sequence of infinite reactions of species \( S_j \) may be given by equation 3–16. The production rates for moments for each of the species \( S_j \) may be found from equation 3–17. Equivalent results may be obtain by performing block-wise summations based on size class, while the reactions may be grouped into reaction classes, such that reactions of a particular class may have similar rate constants [149]. The equations for such block-wise summations are given by equation 3–18 and equation 3–19.

\[
\frac{d[S]}{dt} = K[S] \quad (3-16)
\]

\[
\frac{dM_r}{dt} = \frac{d}{dt} \left( \sum_{j=1}^{\infty} m_j r [S_j] \right) = (m_1 r k_0 - m_1 r k_1 [S_1] + m_1 r k_2 [S_2]) + m_2 r (k_1 [S_1] - (k_{-1} + k_2) [S_2] + k_{-2} [S_3]) + m_3 r (k_2 [S_2] - (k_{-2} + k_3) [S_3] + k_{-3} [S_4]) + \ldots \\
+ m_j r (k_{(j-1)} [S_{(j-1)}] - (k_{-(j-1)} + k_j) [S_j] + k_{-j} [S_{(j+1)}]) + \ldots \\
= m_1 r k_0 + \sum_{j=1}^{\infty} (m_{j+1} r - m_j r) (k_j [S_j] - k_{-j} [S_{j+1}])
\]

\[
\frac{d[S_{i,s}]}{dt} = k_{i,(s-1)} [S_{i,(s-1)}] - (k_{i,-(s-1)} + k_{i,s}) [S_s] + k_{i,-s} [S_{i,(s+1)}]; \ s = 1, 2, \ldots (N_s - 1) \quad (3-18)
\]

\[
\frac{dM_r}{dt} = m_1 r k_0 + \sum_{i=1}^{n_s-1} \sum_{s=1}^{n_s-1} (m_{i,s+1} r - m_{i,s} r) (k_{i,s} [S_{i,s}] - k_{i,-s} [S_{i,s+1}]) \quad (3-19)
\]

Now consider,

\[
(m_{i,s+1} r - m_{i,s} r) = [m_{i,s} + (\Delta m)_{s}]^r - (m_{i,s})^r
\]

\[
= \sum_{p=1}^{\infty} (r C_p) (\Delta m)^p_{s} (m_{i,s})^{(r-p)} + (m_{i,s})^r - (m_{i,s})^r
\]
Hence, the simplification given by equation 3–20 is obtained, where \( m_{i,s} \) may further be calculated from equation 3–21, if the the mass addition \((\Delta m)_B\) in each replicating block is known. It is important to note that the zero\(^{th}\) moment \( M_0 = k_0 \) and that only when \( m_{j+1} \neq m_j \) the moment production term is non-zero. Hence, the moment production rates are affected only by “mass-addition” reactions. Furthermore, mass-additions occur only via changes in carbon atoms, while H atom masses are ignored [149]. If there are \( l_a \) mass-addition reactions in a replicating block, the mass-addition \((\Delta m)_B\), may be given by equation 3–22, where \( \Delta m_l = m_{i,s_l+1} - m_{i,s_l} \). The underlying assumption is that, the total mass addition in each replicating block \((\Delta m)_B\) is constant.

\[
(m_{i,s+1}^r - m_{i,s}^r) = \sum_{p=1}^{\infty} (rC_p)(\Delta m)_s^p(m_{i,s})^{(r-p)} \tag{3–20}
\]

\[
m_{i,s+1} = m_{1,s+1} + (i - 1)(\Delta m)_B \tag{3–21}
\]

\[
(\Delta m)_B = \sum_{l=1}^{l_a} \Delta m_l = \sum_{s=1}^{N_{s_l}} m_{i,s_l+1} - m_{i,s_l} = m_{i+1,s} - m_{i,s} \tag{3–22}
\]

The term \((m_{i,s+1}^r - m_{i,s}^r)\), may further be expressed by equation 3–23, which upon substitution in equation 3–19, gives equation 3–24. Since only mass-addition reactions participate in moment generation, equation 3–24 may be rewritten as equation 3–25, where \( s_l \) is the species index such that mass-addition takes place between species \( S_{s_l} \) and \( S_{s_l+1} \). The equation 3–25 may be rewritten as equation 3–26 by using the variable transformation \( i = b + 1 \).
\[ m_{i,s+1}^r - m_{i,s}^r = (m_{i,s+1} + (i-1)(\Delta m)_B)^r - (m_{1,s} + (i-1)(\Delta m)_B)^r \]  
\[ = [(m_{1,s+1} - (\Delta m)_B) + i(\Delta m)_B]^r - [(m_{1,s} - (\Delta m)_B) + i(\Delta m)_B]^r \] 
\[ = \sum_{p=0}^{r} (rC_p) (m_{1,s+1} - (\Delta m)_B)^{r-p}(i(\Delta m)_B)^p \] 
\[ - \sum_{p=0}^{r} (rC_p) [(m_{1,s} - (\Delta m)_B)^{r-p}(i(\Delta m)_B)]^p \] 
\[ = \sum_{p=0}^{r} [(m_{1,s+1} - (\Delta m)_B)^{r-p} - (m_{1,s} - (\Delta m)_B)^{r-p}](i(\Delta m)_B)^p \]  

\[ \frac{dM_r}{dt} = m_1^r k_0 + \sum_{i=1}^{\infty} \sum_{s=1}^{(N_i-1)} \sum_{p=0}^{r} (rC_p) [(m_{1,s+1} - (\Delta m)_B)^{r-p} - (m_{1,s} - (\Delta m)_B)^{r-p}] \] 
\[ (i(\Delta m)_B)^p (k_{i,s} [S_{i,s}] - k_{i,-s} [S_{i,s+1}]) \]  

\[ \frac{dM_r}{dt} = m_1^r k_0 + \sum_{i=1}^{\infty} \sum_{l=1}^{l_a} \sum_{p=0}^{r} (rC_p) [(m_{1,l+1} - (\Delta m)_B)^{r-p} - (m_{1,l} - (\Delta m)_B)^{r-p}] \] 
\[ (i(\Delta m)_B)^p (k_{i,s_l} [S_{i,s_l}] - k_{i,-s_l} [S_{i,s_l+1}]) \]  

\[ \frac{dM_r}{dt} = m_1^r k_0 + \sum_{l=1}^{l_a} \sum_{p=0}^{r} (rC_p) [(m_{1,l+1} - (\Delta m)_B)^{r-p} - (m_{1,l} - (\Delta m)_B)^{r-p}] \] 
\[ (\Delta m)_B^p \sum_{b=0}^{\infty} (b + 1)^p (k_{b+1,s_l} [S_{b+1,s_l}] - k_{b+1,-s_l} [S_{b+1,s_l+1}]) \]  

Defining new variables, \( \Delta^{[n]_m} m_l \) and \( R_l^{[n]} \), given by equation 3–27 and equation 3–28, respectively, allows the simplification of the moment equation to equation 3–29. Note that the reaction rate variables \( k_{b+1,s_l} \) are functions of non-polymerizing species. This mathematical manipulation is required due to the assumption that all the equations...
are first order and depend only on the concentrations of polymerizing PAH molecules. However, each replicating block, has the same basic reaction mechanism, since, every higher order PAH molecule, reacts in a similar fashion as the species in the first replicating block. Hence, \( k_{b+1,s} = k_{b+2,s} = k_{b+x,s} \); \( x = 1...\infty \). Furthermore, from the assumptions of chemical similarity, the species \( S_{b+1,s} \) can be related to the species \( S_{1,s} \) in the first replicating block as follows: \([PAH]_b = [PAH]_{i_0+3b} \) where \( i_0 \) defines the size of the species \( S_{1,s} \). For example if, \( S_{1,s} = A_1^* \), then \( S_{b+1,s} = A_{i+3}^* \) [149].

\[
\Delta^{[n]}m_t = [(m_{1,t+1} - (\Delta m)_B)^n - (m_{1,t} - (\Delta m)_B)^n] \tag{3–27}
\]

\[
R_t^{[n]} = \sum_{b=0}^{\infty} (b + 1)^p \left( k_{b+1,s} [S_{b+1,s}] - k_{b+1,-s} [S_{b+1,s_{t+1}}] \right) \tag{3–28}
\]

\[
= k_{b+1,s} \sum_{b=0}^{\infty} ((b + 1)^p [S_{b+1,s}]) - k_{b+1,-s} \sum_{b=0}^{\infty} ((b + 1)^p [S_{b+1,s_{t+1}}])
\]

\[
\frac{dM_r}{dt} = m_1^r k_0 + \sum_{p=0}^{r} (rC_p) (\Delta m)_B^p \sum_{l=1}^{l_0} (\Delta^{[r-p]}m_t) R_t^{[p]} \tag{3–29}
\]

The equations of the concentration moments as summarized in [149], are given by equations 3–30 through 3–37. Equation 3–36 gives an example of net flux \( R_t^{[0]} \). For the case of \( R_t^{[j]} \), the zero\(^{th}\) lumped species moment must be replaced by the \( j^{th}\) lumped species moment given by equation 3–37.

\[
\frac{dM_0^{PAH}}{dt} = r_0 \tag{3–30}
\]

\[
\frac{dM_1^{PAH}}{dt} = m_0 r_0 + \sum_{l=1}^{l_0} \Delta m_t^r R_t^{[0]} \tag{3–31}
\]

\[
\frac{dM_2^{PAH}}{dt} = m_0^2 r_0 + \sum_{l=1}^{l_0} \Delta^{[2]}m_t R_t^{[0]} + 2\Delta m_0 \sum_{l=1}^{l_0} \Delta m_t R_t^{[1]} \tag{3–32}
\]
\[
\frac{dM_{r}^{PAH}}{dt} = m_0 r_0 + \sum_{j=0}^{r-1} r C_j (\Delta_c m)^j \sum_{l=1}^{l_c} \Delta^{r-j} m_l R_l^{[j]} \quad (3-33)
\]

\[
\Delta^{[p]} m_l = (m_l - \Delta_c m)^p - (m_{l-1} - \Delta_c m)^p \quad (3-34)
\]

for \( l = 1, 2..., l_c \)

\[
\Delta_c m = \sum_{l=1}^{l_c} m_l = \sum_{l=1}^{l_c} (m_l - m_{l-1}) = m_{i+l_c} - m_i \quad (3-35)
\]

\[
R_l^{[0]} = k_L [C_2H_2] \sum_{i=0}^{\infty} [A_{i0+3i}] - k_- L [H] \sum_{i=0}^{\infty} [A_{i0+3i}C_2H] \quad (3-36)
\]

\[
S_{[PAH]} i = \sum_{i=0}^{\infty} (i + 1)^j [PAH]_{i-3i}^{[j]} \quad (3-37)
\]

### 3.1.4 Particle Coagulation

Frenklach [189] described the coagulation model with the assumption that the collision frequency was independent of the particle size. This methodology extended the work of Smoluchowski for monodisperse initial size distribution. This approach follows a discretization approach with a self-preserving particle size distribution assumption, meaning that an asymptotic solution existed for the reduced particle size distribution [189]. Although the particle size distribution at the time of inception may not be self-preserving [150], this assumption is fundamental to the solution approach. The initial particle-size distribution needs to be narrow in order for a solution to exist, since the time required to attain convergence for a polydisperse distribution is a function of the variance of initial size distribution [189]. The particle coagulation model used in this study is the one presented in Frenklach [187], which has been developed from Method II described in Frenklach and Harris [188]. The coagulation rate is assumed to depend on the Knudsen number. Depending on the value of the Knudsen number, the coagulation process is
Figure 3-4. Process of Soot Coagulation

classified into three separate regimes, the continuum regime, transition regime and the free-molecular regime. The description of the process in these regimes has been discussed in sections 3.1.4.1 through 3.1.4.3, while further details may be found in [187]. Further, the coagulation process is assumed to be resulting from coalescent collisions involving dimerization reactions, such that the spherical shape of the particles is preserved [189]. The process of coagulation has been illustrated in figure 3-4.

3.1.4.1 Continuum regime

The process of coagulation [187] is said to be in continuum regime when $Kn << 1$, that is, when particle sizes are large. For this regime, the collision coefficient is given by equation 3–38. $C$ is the Cunningham slip correction factor and $K_c = \frac{2 k_B T}{3 \eta}$. The correction factor $C$ is a function of Knudsen number and is given by $C = 1 + 1.257Kn$. Substituting these expressions in equation 3–38, gives equation 3–39.

$$
\beta_{i,j}^c = K_c \left( \frac{C_i}{m_i^{\frac{1}{3}}} + \frac{C_j}{m_j^{\frac{1}{3}}} \right) \left( m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}} \right)
$$ (3–38)
The Knudsen number \((Kn)\) may be related to the mass of the soot particle by equation 3–40, where \(Kc' = 2.514\pi\left(\frac{\rho}{\rho_0}\right)^{\frac{1}{3}}\). Substituting these expressions into equation 3–39 gives equation 3–41.

\[
Kn = \frac{\lambda}{d_i/2} = \frac{\lambda}{\frac{1}{2} \left(\frac{6m_i}{\pi \rho}\right)^{\frac{1}{3}}} = 2\lambda \left(\frac{\pi \rho}{6m_i}\right)^{\frac{1}{3}} = \frac{Kc'}{1.257m_i^{\frac{1}{3}}}
\]

(3–40)

\[
\beta_{i,j} = Kc \left(\frac{1}{m_i^{\frac{1}{3}}} + \frac{1}{m_j^{\frac{1}{3}}}\right) \left(m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}}\right) + KcKc' \left(\frac{1}{m_i^{\frac{2}{3}}} + \frac{1}{m_j^{\frac{2}{3}}}\right) \left(m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}}\right)
\]

(3–41)

If we substitute the above expressions of \(\beta_{i,j}\) in the expressions for coagulation rates, we can obtain an expression of the rates in terms of the fractional moments of the soot particles, as given by equation 3–42.

Consider first the coagulation rate of formation of zero\(^{th}\) moment. Its expression is given as equation 3–42, which may further be simplified to equation 3–43. Substituting normalized size-moments \(\mu_r = \frac{M_r}{M_0}\) in equation 3–43 gives equation 3–44.

\[
G_0 = \frac{dM_0}{dt} = -\frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \beta_{i,j} N_i N_j
\]

(3–42)

\[
= -\frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left[ Kc \left(\frac{1}{m_i^{\frac{1}{3}}} + \frac{1}{m_j^{\frac{1}{3}}}\right) \left(m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}}\right) + KcKc' \left(\frac{1}{m_i^{\frac{2}{3}}} + \frac{1}{m_j^{\frac{2}{3}}}\right) \left(m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}}\right) \right] N_i N_j
\]

\[
= -\frac{1}{2} Kc \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left[ \left(2 + 2m_i^{\frac{1}{3}} m_j^{\frac{1}{3}}\right) + Kc' \left(2m_i^{\frac{2}{3}} + 2m_i^{\frac{1}{3}} m_j^{\frac{2}{3}}\right) \right] N_i N_j
\]
\[ G_0^c = -\frac{1}{2} K_c \left[ \left( 2M_0^2 + M_{\frac{1}{3}} M_{\frac{2}{3}} + M_{\frac{2}{3}} M_{\frac{1}{3}} \right) + K_c \left( 2M_{\frac{2}{3}} M_0 + 2M_{\frac{1}{3}} M_{\frac{2}{3}} \right) \right] \] (3–43)

\[ = -K_c \left[ \left( M_0^2 + M_{\frac{1}{3}} M_{\frac{2}{3}} \right) + K_c \left( M_{\frac{2}{3}} M_0 + M_{\frac{1}{3}} M_{\frac{2}{3}} \right) \right] \]

\[ G_0^c = -K_c M_0^2 \left[ \left( 1 + \mu_{\frac{1}{3}} \mu_{\frac{2}{3}} \right) + K_c \left( \mu_{\frac{2}{3}} + \mu_{\frac{1}{3}} \mu_{\frac{2}{3}} \right) \right] \] (3–44)

Similarly, the \( r \)th coagulation moment rate may be expressed by equation 3–45.

Substituting the definition of concentration moment and size moments into equation 3–45, gives equation 3–46 and equation 3–47, respectively.

\[ G_r^c = \frac{dM_r}{dt} = \frac{1}{2} \left( \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=2}^{r-1} \left[ K_c \left( 1 + m_i \mu_{\frac{1}{3}} m_j \mu_{\frac{2}{3}} + m_j \mu_{\frac{2}{3}} m_i \mu_{\frac{1}{3}} + 1 \right) + K_c \left( m_i \mu_{\frac{1}{3}}^r + m_i \mu_{\frac{2}{3}}^r + m_j \mu_{\frac{2}{3}}^r + m_j \mu_{\frac{1}{3}}^r \right) \right] \right) \]

\[ r C_k \right) \] (3–45)

\[ G_r^c = -\frac{1}{2} K_c \sum_{k=2}^{r-1} \left[ \left( M_k M_{r-k} + M_{k+\frac{1}{3}} M_{r-k-\frac{1}{3}} + M_{k-\frac{1}{3}} M_{r-k+\frac{1}{3}} + M_k M_{r-k} \right) + K_c \left( M_k M_{r-k} + M_{k+\frac{1}{3}} M_{r-k-\frac{2}{3}} + M_{k-\frac{2}{3}} M_{r-k+\frac{1}{3}} + M_k M_{r-k-\frac{1}{3}} \right) \right] \] (3–46)

\[ G_r^c = -\frac{1}{2} K_c \left( M_0 \right)^2 \sum_{k=2}^{r-1} \left[ \left( 2\mu_{k+\frac{1}{3}} \mu_{r-k-\frac{1}{3}} + \mu_{k-\frac{1}{3}} \mu_{r-k+\frac{1}{3}} + \mu_{k+\frac{1}{3}} \mu_{r-k-\frac{2}{3}} + \mu_{k-\frac{2}{3}} \mu_{r-k+\frac{1}{3}} + \mu_{k+\frac{1}{3}} \mu_{r-k-\frac{1}{3}} \right) + K_c \left( \mu_{k-\frac{1}{3}} \mu_{r-k} + \mu_{k+\frac{1}{3}} \mu_{r-k-\frac{2}{3}} + \mu_{k-\frac{2}{3}} \mu_{r-k+\frac{1}{3}} + \mu_{k+\frac{1}{3}} \mu_{r-k-\frac{1}{3}} \right) \right] \] (3–47)

### 3.1.4.2 Free-molecular regime

The expression for collision coefficient in free-molecular regime \((Kn \gg 1)\) is given by equation 3–48, where \(K_f\) may be obtained from equation 3–49. Substituting these equations for the free-molecular regime into the zero\(^{th}\) coagulation moment rate equation
gives equation 3–50. In equation 3–50, due to the $\sqrt{m_i + m_j}$ term, it is impossible to write the above expression for $G_0^f$ in terms of the fractional moments. Instead, a new function called the “grid function” was defined, which can be described in terms of moments and can be interpolated for grid function values. The grid function ($f_i$) is given by equation 3–51 and equation 3–52. The grid functions may further be interpolated between, the grid function values for $f_0$, $f_1$, and $f_2$, which may be evaluated from equations 3–53 through 3–55. Similarly, the expression for the $r^{th}$ coagulation moment rate is given by equation 3–56. Further details may be found in [187].

$$\beta_{i,j}^f = K_f \sqrt{\frac{1}{m_i} + \frac{1}{m_j} \left( m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}} \right)^2} \quad (3-48)$$

where,

$$K_f = \epsilon \sqrt{\frac{6k_B T}{\rho}} \left( \frac{3}{4\pi \rho} \right)^{\frac{1}{6}} \quad (3-49)$$

$$G_0^f = \frac{dM_0}{dt} = -\frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \beta_{i,j} N_i N_j \quad (3-50)$$

$$= -\frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left[ K_f \sqrt{\frac{1}{m_i} + \frac{1}{m_j} \left( m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}} \right)^2} \right] N_i N_j$$

$$= -\frac{1}{2} K_f \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left[ \left( m_i + m_j \right)^{\frac{1}{2}} m_i^{\frac{1}{2}} m_j^{\frac{1}{2}} (m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}})^2 \right] N_i N_j$$

$$f_i = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left[ (m_i + m_j)^{\frac{1}{2}} m_i^{\frac{1}{2}} m_j^{\frac{1}{2}} (m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}})^2 \right] N_i N_j \quad (3-51)$$

$$f_i^{(x,y)} = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left[ (m_i + m_j)^{\frac{1}{2}} m_i^{\frac{1}{2}} m_j^{y} (m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}})^2 \right] N_i N_j \quad (3-52)$$
\[ f_0 = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [m_i^\frac{3}{2} m_j^\frac{1}{2} (m_i^\frac{1}{2} + 2m_i^\frac{1}{2} m_j^\frac{1}{2} + m_j^\frac{3}{2})] N_i N_j \]  
\[ = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (m_i^\frac{3}{2} m_j^\frac{1}{2} + 2m_i^\frac{1}{2} m_j^\frac{3}{2} + m_i m_j^\frac{3}{2}) N_i N_j \]  
\[ = 2[M_M^2 + M_M M_M^2] \]  

\[ f_1 = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [(m_i + m_j)m_i^\frac{1}{2} m_j^\frac{1}{2} (m_i^\frac{1}{2} + 2m_i^\frac{1}{2} m_j^\frac{1}{2} + m_j^\frac{3}{2})] N_i N_j \]  
\[ = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (m_i + m_j)(m_i^\frac{1}{2} m_j^\frac{1}{2} + 2m_i^\frac{1}{2} m_j^\frac{3}{2} + m_i m_j^\frac{3}{2}) N_i N_j \]  
\[ = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [(m_i^\frac{1}{2} m_j^\frac{3}{2} + 2m_i^\frac{1}{2} m_j^\frac{5}{2} + m_i m_j^\frac{7}{2})] N_i N_j \]  
\[ = 2[M_M M_M^2 + M_M^2 M_M^2 + 2M_M M_M] \]  

\[ f_2 = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [(m_i + m_j)^2 m_i^\frac{1}{2} m_j^\frac{1}{2} (m_i^\frac{1}{2} + 2m_i^\frac{1}{2} m_j^\frac{1}{2} + m_j^\frac{3}{2})] N_i N_j \]  
\[ = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (m_i + m_j)(m_i^\frac{1}{2} m_j^\frac{1}{2} + 2m_i^\frac{1}{2} m_j^\frac{3}{2} + m_i m_j^\frac{3}{2}) N_i N_j \]  
\[ = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (m_i + m_j) [(m_i^\frac{1}{2} m_j^\frac{1}{2} + 2m_i^\frac{1}{2} m_j^\frac{3}{2} + m_i m_j^\frac{3}{2})] N_i N_j \]  
\[ = 2[M_M M_M^2 + M_M^2 M_M^2 + 2M_M^2 M_M^2 + M_M M_M^2 M_M^2] \]
\[
G_r = \frac{dM_r}{dt} = \frac{1}{2} \left( \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=2}^{r-1} \beta_{i,j}^f(rC_k)m_i^r m_j^{r-k} N_i N_j \right) \tag{3-56}
\]

\[
= \frac{1}{2} \left( \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=2}^{r-1} \left[ K_f \sqrt{m_i + m_j} m_i^{1/2} m_j^{1/2} (m_i^{1/4} + m_j^{1/4})^2 \right] (rC_k)m_i^r m_j^{r-k} N_i N_j \right)
\]

\[
= \frac{1}{2} \sum_{k=2}^{r-1} (rC_k)f_{1/2}^{k-1/2}r^{k-1/2} N_i N_j
\]

3.1.4.3 Transition regime

The expression of rates for the transition regime [187] may be obtained from the geometric mean of the limiting cases of continuum and free-molecular regimes, given by equation 3–57.

\[
G_r^t = \frac{G_r^f G_r^c}{G_r^f + G_r^c} \tag{3-57}
\]

3.1.4.4 Interpolative closure

The fractional moments in the expressions for moment rates were interpolated between the whole order moments obtained from the moment rate expressions \(G_0, G_1...G_r\).

The positive-side interpolation uses the lagrange interpolation technique between the whole order size-moments. The general \(n^{th}\) order interpolation at point \(x\) between grid points \(x_i\) for known \(y_i = y(x_i)\) is given by equation 3–58, where the polynomials \(l_i(x)\), may be evaluated from equation 3–59. The interpolation of \(\mu(p)\) follows the logarithmic lagrange interpolation given by equations 3–60 through 3–62.

\[
P_n(x) = \sum_{i=1}^{n} l_i(x) y_i \tag{3-58}
\]

\[
l_i(x) = \prod_{j=1}^{n} \frac{x - x_j}{x_i - x_j} \tag{3-59}
\]

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\[ \log (\mu_p) = L_P (\log (\mu_0), \log (\mu_1), \ldots, \log (\mu_{r_{\text{max}}})) \quad ; \quad p > 0 \quad (3-60) \]

\[ \log (\mu_p) = P_n (p) = \sum_{i=1}^{n} l_i (p) [\log (\mu_i)] \quad (3-61) \]

\[ \mu_p = 10^{P_n(p)} = \prod_{i=1}^{n} [\mu_i]^{l_i(p)} \quad (3-62) \]

The grid functions \( f_l \) and \( f_l(x,y) \) may be interpolated using a similar approach.

Further details on interpolative closure may be found in [149, 187].

### 3.1.5 Particle Aggregation

The aggregation of particles through non-coalescent or agglomerative collisions results in the formation of self-similar fractal structures, as shown in figure 3-5. This part of the submodel was omitted from the analysis, since aggregation would only occur at high soot concentrations, however, we are interested in modeling the flameless combustion regime, with low soot concentrations. Details on the fractal aggregation submodel may be found in the work of [165, 196, 198–200].

### 3.1.6 Surface Chemistry - Growth and Oxidation

The soot surface chemistry is modeled by a reduced HACA mechanism. The process has been depicted in figure 3-6. The reaction data for the HACA mechanism has been
Figure 3-6. Process of Soot Surface Reactions

taken from Appel et al. [148]. Appel et al. [148] proposed changes to the reduced HACA mechanism for soot surface growth submodel of Kazakov et al. [158]. The submodel utilizes the technique of linear lumping described in [190, 207]. The method of moments [149, 187–189] is used to derive information regarding the particle-size distribution. The relevant procedure and equations have been discussed in detail in section 3.1.3.

The $\alpha$ parameter (represents soot particle surface ageing/annealing), in the surface growth model was initially considered to be a constant [150]. Later, it was modified to include a functional dependence on the maximum flame temperature [158]. Appel et al. [148] further included dependence of the $\alpha$ on the particle size $\mu_1$ and local flame temperature $T$, as given by equation 3–63, where the constants $a$ and $b$ were given by $a = 12.65 - 0.00563T$ and $b = -1.38 + 0.00068T$ [148].

$$\alpha = \tanh \left( \frac{a}{\log(\mu_1)} + b \right) \quad (3–63)$$

The reduced set of heterogeneous surface reactions (HACA mechanism) between the soot particles and gas phase species may be found in Appel et al. [148], Revzan et al. [208]. These reactions add or remove mass from the soot surface, resulting in growth or oxidation of the particle. As a result, the size class of an isolated soot particle may shift.
down or up by the difference $\Delta m$ in the size bin of the PSDF. In the surface reactions, 
$C_s[i] - H$ represents the active arm-chair site that may undergo surface reactions while 
$C_s[i]^* \equiv$ represents the active radical site on the surface of a soot particle. Note that the 
surface reactions, depend on the concentrations of the gas-phase species and the total 
active reaction sites $[X_i^{site}]$ on a soot particle. The average surface density of the reaction 
sites may be given by equation 3–68.

The soot mass, surface area and volume fraction are related to the size moments [208]. The equations for the soot mass, surface area $s$ and soot volume fraction $f_v$ may 
be calculated from equations 3–64, 3–65 and 3–67, respectively. From equation 3–64 for 
soot mass, the particle diameter ($d_i$), may be determined as given by equation 3–66, where 
$C_d = \left[ \frac{6mC}{\rho \pi} \right]^{\frac{1}{3}}$. Substituting the expression for $d_i$ from equation 3–66 in equation 3–65, 
allows calculating the expression for $s$ in terms of the moments.

$$m_i m_C = \frac{\pi}{6} d_i^3 \quad (3–64)$$

$$s = \sum_i N_{i} s_i = \pi \sum_i N_i d_i^2 = \pi \langle d_i^2 \rangle N_{tot} \quad (3–65)$$

$$= \pi C_d^2 \mu_2 M_0$$

$$d_i = \left[ \frac{6m_i m_C}{\rho \pi} \right]^{\frac{1}{3}} = m_i^{\frac{1}{3}} C_d \quad (3–66)$$

$$f_v = \sum_i N_{i} v_i = \frac{\pi}{6} \sum_i N_i D_i^3 = \frac{\pi}{6} \langle D_i^3 \rangle N_{tot} \quad (3–67)$$

$$= \frac{\pi}{6} C_d^3 \mu_1 M_0$$
\[
< [X_i^{\text{site}}] > = \frac{\alpha \chi_s}{N_A} = \frac{\sum_{i=1}^{\infty} X_i^{\text{site}} s_i N_i}{\sum_{i=1}^{\infty} s_i N_i}
\] (3–68)

\(\chi_s\) is the number of active sites on the soot particle surface, \(\alpha\) is the steric hindrance factor and \(s\) is the surface area. The concentration for \(C_s[i]\) can be determined from application of quasi-steady-state approximation (QSSA).

The total active sites (\([X_i^{\text{site}}]\)) available are a sum of the sites \(C_s[i] - H\) as well as the radical sites \(C_s[i]^{\ast}\). The average over the entire distribution of particles with number density \(N_i\) and surface area \(s_i\), gives the averaged active site coverage (\(< [X_i^{\text{site}}] >\)), as given by equation 3–68. The concentration of \(C_s[i] - H\) is given by equation 3–69, while equation 3–71 allows calculation of \(C_s[i]^{\ast}\). The radical sites are assumed to be extremely reactive and hence, quasi-equilibrated. Hence, the rate constant \(k_s = k_{s_j} X_j [X_i^{\text{site}}]\) where \(X_j\) is the gas phase species reacting with the active reaction-site \(X_i^{\text{site}}\) of the \(i\)th soot particle. The reaction being the \(j\)th HACA reaction proceeding at a rate \(k_{s_j}\). The value of \(\Delta m\) is 2 for acetylene reactions, -2 for reactions of \(O_2\) and -1 for OH reactions.

\[
\left[ C_s[i] - H \right] = \frac{\chi_s}{N_A} \alpha s
\] (3–69)

\[
\frac{d \left[ C_s[i]^{\ast} \right]}{dt} = k_{S1} \left[ C_s[i] - H \right] [H] - k_{-S1} \left[ C_s[i]^{\ast} \right] [H_2] + k_{S2} \left[ C_s[i] - H \right] [OH] - k_{-S2} \left[ C_s[i]^{\ast} \right] [H_2O] - k_{S3} \left[ C_s[i]^{\ast} \right] [H] - k_{S4} \left[ C_s[i]^{\ast} \right] [C_2H_2] - k_{S5} \left[ C_s[i]^{\ast} \right] [O_2] = 0
\] (3–70)

\[
\left[ C_s[i]^{\ast} \right] = \frac{\left[ C_s[i] - H \right] (k_{S1} [H] + k_{S2} [OH])}{k_{-S1} [H_2] + k_{-S2} [H_2O] + k_{S3} [H] + k_{S4} [C_2H_2] + k_{S5} [O_2]} = k_{\text{ratio}} \left[ C_s[i] - H \right]
\] (3–71)

where \(k_{\text{ratio}} = \frac{(k_{S1} [H] + k_{S2} [OH])}{k_{-S1} [H_2] + k_{-S2} [H_2O] + k_{S3} [H] + k_{S4} [C_2H_2] + k_{S5} [O_2]}\).
The model for moment contributions from the surface growth process has been discussed in \cite{149, 187}. The surface growth process is a sequential growth process, such that the particle size class may shift between adjacent bins based on the mass-addition or removal by specified monomer units. The equations for such a surface growth between size classes i-1, i and i+1, as described in \cite{187}, are given by equation 3–73 and equation 3–74. The rate constant \((k_s)\) used in these equations may be evaluated using equation 3–72.

Substituting the definition of rate constant \((k_s)\) from equation 3–72 and surface area \((s)\) from equation 3–65 into equation 3–74, allows calculation of the surface growth moment production rate contributions from the individual species. The moment rate contributions for surface growth from species \(C_2H_2\), \(OH\) and \(O_2\), may be evaluated based on equation 3–75 through equation 3–77.

\[
k_s = k_{sj} [X_j] [X_i^{\text{site}}] = k_{sj} [X_j] \frac{X_s}{N_A} s \alpha \quad (3–72)
\]

\[
\frac{dN_1}{dt} = -\frac{k_s N_1 s_1}{\Delta m}
\]

\[
\frac{dN_i}{dt} = \frac{k_s}{\Delta m} (N_{i-1}s_{i-1} - N_is_i) ; \ i = 2, 3...
\]

\[
W_r = \frac{dM_r^s}{dt} \quad (3–74)
\]

\[
= -\frac{k_s}{\Delta m} \left[ \sum_{i=2}^{\infty} (m_{i-1} + \Delta m)^r (N_{i-1}s_{i-1} - m_i^r N_is_i) \right] ; \ i = 2, 3...
\]

\[
= -\frac{k_s}{\Delta m} \left[ \sum_{i=1}^{\infty} \left( \sum_{k=0}^{r-1} (rC_k) m_i^k \Delta m^{r-k} N_is_i + (m_i)^r (\Delta m)^0 N_is_i \right) - \sum_{i=1}^{\infty} (m_i^r N_is_i) \right]
\]

\[
= -\frac{k_s}{\Delta m} \sum_{i=1}^{\infty} \left( \sum_{k=0}^{r-1} (rC_k)m_i^k \Delta m^{r-k} N_is_i \right) ; \ i = 1, 2, 3...
\]
\[ W_{rC_2H_2} = -\frac{k_{S4} [C_2H_2] \alpha \chi_s \left[ C_s[^i] \right]^* \pi C_d^2}{\Delta m} \left( \sum_{k=0}^{r-1} (rC_k)M_{l+\frac{2}{3} soot}(2)^{r-k} \right) ; i = 1, 2, 3 \ldots \quad (3–75) \]

\[ W_{rO_2} = -\frac{k_{S5} [O_2] \alpha \chi_s \left[ C_s[^i] \right]^* \pi C_d^2}{\Delta m} \left( \sum_{k=0}^{r-1} (rC_k)M_{l+\frac{2}{3} soot}(-2)^{r-k} \right) ; i = 1, 2, 3 \ldots \quad (3–76) \]

\[ W_{rOH} = -\frac{k_{S6} \gamma_{OH} \sqrt{\frac{\pi k_B T}{2m_{OH}}} [OH] \pi C_d^2}{\Delta m} \left( \sum_{k=0}^{r-1} (rC_k)M_{l+\frac{2}{3} soot}(-1)^{r-k} \right) ; i = 1, 2, 3 \ldots \quad (3–77) \]

The collisional efficiency \((\gamma_{OH})\) which is the ratio of the experimental to collisional theory rate constant for OH reactions, was taken from Neoh et al. [206]. The surface processes do not change the number density, but only affect the particle size, hence, the zero\(^{th}\) moment is not affected. As a consequence of the surface reactions, some of the surface species are consumed, and hence correction terms need to be added to the gas phase species balance equations, at every time step. The correction terms for the species production rates are calculated from the total mass growth of soot particles due to surface growth (which is a function of \(W_1\)). Only species \(C_2H_2\), \(OH\) and \(O_2\) contributed to mass addition or removal from the soot particles. An additional term accounts for production rates of species involved in the chemistry that accounts for depletion or appearance of \([C_s[^i] \cdot \cdot \cdot] \) and \([C_s[^i] - H]\) sites. These reactions do not contribute towards mass addition or removal from soot particles, especially since mass of H atoms has been neglected in the analysis, and therefore, need to be accounted for by an additional chemical kinetic production rate term. Defining two constants \(C_a\) and \(C_r\) given by \(C_a = \alpha_s \chi_s \pi C_d^2 M_0\) and \(C_r = k_{ratio} C_a\), allows simplification of the equations. As an example, consider the production term for \(H_2O\),
\[ \dot{\omega}_{H_2O}^{\text{corr.}} = k_{S2f}[OH] \left[ C_s^{[i]} - H \right] - k_{S2r}[H_2O] \left[ C_s^{[i]} \ast \right] \\
= (k_{S2f}[OH] - k_{S2r}[H_2O]k_{\text{ratio}}) \frac{X_s}{N_A} \alpha \left( \pi C_a^2 \mu_3^2 M_0 \right) \\
= (k_{S2f} C_a - k_{S2r} C_r) \frac{\mu_3^2}{N_A} \]

These correction terms for the individual species have been summarized in equations 3–78 through 3–84. Although the formalism of the approach for surface growth has been presented in [149], the HACA mechanism itself was modified first in Kazakov et al. [158], and then in Appel et al. [148]. The correction terms and the kinetic parameters for the HACA reactions presented here (including the reaction rates for the reverse reactions) have been taken from Revzan et al. [208].

\[ \dot{\omega}_{C_2H_2}^{\text{corr.}} = - \frac{W_1 C_2H_2}{2 N_A} \quad (3–78) \]

\[ \dot{\omega}_{O_2}^{\text{corr.}} = - \frac{W_1 O_2}{2 N_A} \quad (3–79) \]

\[ \dot{\omega}_{OH}^{\text{corr.}} = (k_{S2r}[H_2O]C_r - k_{S2f}[OH]C_a) \frac{\mu_3^2}{N_A} + \frac{W_1 OH}{N_A} \quad (3–80) \]

\[ \dot{\omega}_H^{\text{corr.}} = ((k_{S1f}[H_2] + k_{S4f}[C_2H_2]) C_r - k_{S1f}[H]C_a - k_{S3f}[H]C_r) \mu_3^2 \quad (3–81) \]

\[ \dot{\omega}_{H_2}^{\text{corr.}} = (k_{S1f}[H]C_a - k_{S1r}[H_2]C_r) \frac{\mu_3^2}{N_A} \quad (3–82) \]

\[ \dot{\omega}_{H_2O}^{\text{corr.}} = (k_{S2f}[OH]C_a - k_{S2r}[H_2O]C_r) \frac{\mu_3^2}{N_A} \quad (3–83) \]

\[ \dot{\omega}_{CO}^{\text{corr.}} = - \frac{(W_1 O_2 + W_1 ^{OH})}{N_A} \quad (3–84) \]
3.1.6.1 PAH condensation

A sub-group of surface reactions occurring simultaneously, are those of PAH molecules condensing on the surface of soot particles. The reaction scheme has been depicted in figure 3-6. The condensation process can be written in terms of smoluchowski equation for particle coagulation, given by equation 3–85. The equations given in this section have been taken from Frenklach and Wang [149], Balthasar [209].

\[
\frac{dN_1}{dt} = -\sum_{j=1}^{\infty} \beta_{1,j} N_1 N_j^P 
\]

\[
\frac{dN_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} \beta_{j,i-j} N_j^P N_{i-j}^S - \sum_{j=1}^{\infty} \beta_{i,j} N_i^S N_j^P; \ i = 2, 3, ...
\]

where \( N_i^P \) and \( N_j^S \) represent the number densities of PAH and soot particles respectively. The above equation can further be expressed in terms of moments as in equation 3–86, following procedure outlined in section 3.1.4. The collision frequency for surface condensation (\( \beta_{i,j}^{sc} \)) can be calculated from equation 3–87, while the mass and radius of soot particles may be calculated from equation 3–88 and equation 3–89, respectively. The reduced mass for the collision of PAH molecules and soot particle is calculated from equation 3–90, based on the assumption that \( m_i^S >> m_j^P \).

\[
\frac{dM_r}{dt} = \frac{1}{2} \left( \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=2}^{r-1} \beta(rC_k)m_i^r m_j^{r-k} N_i^S N_j^P \right); \ i = 1, 2, 3, ...
\]

\[
\beta_{i,j}^{sc} = 2.2 \sqrt{\frac{\pi k_B T}{2 \mu_{i,j}}} (d_i^S + d_j^P)^2
\]

where the PAH molecule diameter is given by \( d_j^P = d_A \sqrt{m_j^{P^{\frac{1}{2}}}} \). The width of an aromatic ring (\( d_A \)) is given by \( d_A = \sqrt{3}L_{C-C} \) where \( L_{C-C} \) is the C-C bond length in PAH molecules, with a value of 1.39 nm [149].
\[ m_i m_C = \frac{4\pi}{3} r_i^3 \]  
\[ r_i^2 = \left[ \frac{3(im_1)(m_C)}{4\rho\pi} \right]^{\frac{1}{3}} \]  
\[ \mu_{i,j} = \frac{1}{m_i S} + \frac{1}{m_j P} = \frac{1}{m_j P} \]  
(3–90)

New constant \( C_h \) and \( C_s \) are defined for convenience, by equations 3–91 and 3–92.

Substituting the results from these equations and equation 3–90 in equation 3–87 gives equation 3–93. Substituting the expression for \( \beta_{i,j}^{sc} \) in the moment equation gives equation 3–94, which may further be simplified to equation 3–95.

\[ C_h = \left[ \frac{m_C}{\rho\pi} \right]^{\frac{1}{3}} \]  
(3–91)

\[ C_s = d_A \sqrt{\frac{2}{3}} \]  
(3–92)

\[ \beta_{i,j}^{sc} = 2.2 \sqrt{\frac{\pi k_B T}{2m_C}} (m_j P)^{-\frac{1}{2}} \left[ C_h (m_i S)^{\frac{1}{3}} + C_s (m_j P)^{\frac{1}{2}} \right]^2 \]

\[ = 2.2 \sqrt{\frac{\pi k_B T}{2m_C}} \left[ C_s^2 (m_j P)^{-\frac{1}{2}} (m_i S)^{\frac{1}{3}} + 2C_sC_h (m_j P)^{\frac{1}{2}} (m_i S)^{\frac{1}{3}} + C_h^2 (m_j P)^{\frac{1}{2}} (m_i S)^{\frac{1}{3}} \right] \]

\[ \frac{dM_r}{dt} = \frac{1}{2} \left( \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=2}^{r-1} \beta_{i,j}^{sc}(rC_k)m_i r m_j r^{-k} N_i S N_j P \right) \]  
(3–94)

\[ W_r^{sc} = \frac{dM_r}{dt} = \frac{1}{2} \sum_{k=2}^{r-1} \beta_{i,j}^{sc}(rC_k)m_i r m_j r^{-k} N_i S N_j P \]  
(3–95)

\[ = \frac{1}{2} \sqrt{\frac{\pi k_B T}{2}} \sum_{k=2}^{r-1} (rC_k) \left[ C_s^2 M_{r-k-\frac{1}{2}} M_{k+\frac{1}{2}} S + 2C_sC_h M_{r-k} M_{k+\frac{1}{2}} S + C_h^2 M_{r-k+\frac{1}{2}} M_{k} S \right] \]
3.1.6.2 Particle nucleation

Previously, particle nucleation was modeled by assuming collision between PAH molecules (dimerization), larger aromatics or benzene particles [148–150]. The infinite reaction sequence was broken down into polymerization blocks connected via irreversible reactions [207]. Frenklach and Wang [150] described the nucleation process using method of linear lumping of the sequential growth HACA reaction mechanism. The reaction set was approximated as a unimolecular reaction sequence of fused ring molecules. The subsequent dimerization of these ring structures in free molecular coagulation processes results in further growth of these molecules. Post-dimerization three-dimensional clusters were treated as soot particles. They also discussed that the size discrepancy between PAH molecules and the soot particles, was an indication of the importance of coagulation process in particle growth process and that nucleation alone, could not explain such a discrepancy. Moreover, the HACA sequential growth model for nucleation failed to predict the concentrations of soot nuclei observed in the experiments [203]. Subsequently, the coagulation of two pyrene molecules in dimerization reactions was studied Schuetz and Frenklach [203], and it was found that collision of these pyrene molecules is stabilized by a mechanism of energy storage in internal rotors, resulting in sufficiently long lifetimes for nucleation to occur [203]. Therefore, this study uses the approach of dimerization of pyrene molecules to model nucleation [208]. The smoluchowski’s equation for such a coagulation process resulting in nucleation is given by equation 3–96.

\[
\frac{dN_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} \beta_{i,j-j} P_i N_{i-j} P - \sum_{j=1}^{\infty} \beta_{i,j} N_i P N_j P
\]  

(3–96)

Note, from figure 3-4 that, the first and second terms of the smoluchowski’s equation represent the production and consumption of nuclei, respectively. The nuclei, once formed, may react with other soot particles to form larger soot particles. The consumption term of the nucleus of size \( i_0 \), signifies this phenomenon. However, this is essentially the growth process, and has already been accounted for in coagulation model. Hence, the second term
may be neglected for the nucleation process. The Smoluchowski’s equation for nucleation, reduces to equation 3–97. Multiplying this equation with \((m_i^P)^r\) gives equation 3–98, which is the moment equation for nucleation.

\[
\frac{dN_{i}^{nuc}}{dt} = \frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{i-1} \beta_{i,j} N_i^P N_{i-j}^P \tag{3–97}
\]

\[
R_r = \frac{dM_i}{dt} = \frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (m_i + m_j)^r \beta_{i,j} N_i^P N_j^P \tag{3–98}
\]

The collision frequency for nucleation \(\beta_{i,j}^{nuc}\) is also a function of \(Kn\). For small particles such as PAH molecules \((Kn >> 1)\), the expressions for free-molecular regime may be applied, with the assumption that they belong to the same size class \((i = j = i_0)\). Applying these assumptions gives the expression for \(\beta_{i,j}^{nuc}\) given in equation 3–99. The constant \(K_f\) may be calculated from \(K_f = \epsilon \sqrt{\frac{6k_BT}{\rho}} \left(\frac{3}{4\pi \rho}\right)^{\frac{1}{6}}\). Substituting these expressions into equation 3–98 gives equation 3–100 and equation 3–101 for the \(r^{th}\) and the zero\(^{th}\) moment rates for nucleation, respectively. The equations described in this section may be found in [208].

\[
\beta_{i,j}^{nuc} = K_f \sqrt{\frac{1}{m_i} + \frac{1}{m_j} (m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}})^2} \tag{3–99}
\]

\[
= K_f \sqrt{\frac{2}{m_{i_0}} (4m_{i_0}^{\frac{2}{3}})} = 4\sqrt{2}K_fm_{i_0}^{\frac{1}{6}}
\]

\[
R_r^f = \frac{dM_{r}^{nuc}}{dt} = \frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} 4\sqrt{2}m_i^{\frac{1}{6}} (m_i + m_j)^r N_i^P N_j^P \tag{3–100}
\]

\[
= 2\sqrt{2} (2m_{i_0})^{r+\frac{1}{6}} (N_{i_0}^P)^2
\]

\[
= (2m_{i_0})^r R_{0}^f = (2m_{i_0}) R_{r-1}^f
\]
\[
R_{0f} = 2\sqrt{2} \left(2m_{i0}\right)^{\frac{1}{2}} \left(N_{i0}\right)^2
\]  

(3–101)

### 3.1.7 Prediction of Smoke Number (SN)

The expressions for correlation of Smoke Number and soot mass density \(m_s = \rho_f \nu\), in \(mgm^{-3}\) were taken from Colket III et al. [141]. The volume was based on conversion to atmospheric pressure and 298 K [141]. The SN can be evaluated from equation 3–102 and equation 3–103, if \(m_s\) is known. Similarly, \(m_s\) could be calculated from SN using equation 3–104 and equation 3–105.

\[
SN = -1.8743m_s^2 + 12.117m_s; m_s < 2.5
\]  

(3–102)

\[
SN = -12.513m_s^{0.4313}; m_s > 2.5
\]  

(3–103)

\[
m_s = 3.232 \left[ 1 - \left(1 - \frac{SN}{19.58}\right)^{0.5}\right]; m_s < 18.7
\]  

(3–104)

\[
m_s = 0.002751SN^{-2.319}; m_s > 18.7
\]  

(3–105)

### 3.2 Combustor CSTR Network Model

#### 3.2.1 Software

In order to model the detailed gas phase kinetics, the semiclosed cycle (SCC) gas turbine combustor has been modeled using a CSTR network. The code was written using open source software Cantera v.1.7 [210] using its C++ interface, and it was compiled using g++ compiler v.4.2.3 on a Linux(Ubuntu distribution) machine. The machine hardware configuration was a Dell Dimension C521 system with a AMD Athlon(tm) 64 X2 Dual Core Processor 4400+, 2 GB RAM.
3.2.2 Model

A network of CSTRs, as shown in figure 3-8, was used to model the combustor. The model consisted of two CSTRs, the combustor and the flow-split. Four reservoirs, namely, fuel inlet, air inlet, igniter and exhaust, formed the sources or sinks for thermo-fluid interactions with the combustor and flow-split reactors. The states of the reservoirs were time-invariant and hence, these were used to specify the entry states of the fluid streams and the exit pressure. The model used mass flow regulators (MFRs) in order to simulate constant mass flow conditions for the inlet fluid streams, irrespective of the combustor transients. The exhaust gas from the combustor reactor as well as the flow-split reactor was fed downstream through valves $v_1$ and $v_2$, respectively. The exit mass flow rate through the valves was controlled by the differential pressure between the reactor and the downstream condition. It may be noted that, unless the pressure is kept constant across the valves, the flow of EGR stream may not occur due to adverse pressure gradient. Additionally, in a practical system, the EGR stream may undergo a sequence of processes such as expansion, recuperation, water extraction, compression, etc.

3.2.3 Governing Equations

For the given reactor network, the detailed kinetics are solved in parallel with the flow simulations. The schematic for the inputs to the model is depicted in the figure 3-9. For a single stream transient CSTR network model with only one stream each, for inlet and exit, the governing conservation equations [210] may be written as:

- **Species Conservation:**
  \[
  \left( \frac{dm_j}{dt} \right)_{CV} = \dot{m}_{in} Y_{j,in} - \dot{m}_{ex} Y_{j,ex} + \bar{M}_j \dot{V}_R \dot{\omega}_j + A_R \dot{s}_j
  \]  
  (3–106)

- **Total Mass Conservation:**
  \[
  \left( \frac{d(\rho V_R)}{dt} \right)_{CV} = \dot{m}_{in} - \dot{m}_{ex}
  \]  
  (3–107)

- **Energy Conservation:**
\[
\left( \frac{dU}{dt} \right)_{CV} = \dot{m}_{in} h_{in} - \dot{m}_{ex} h_{ex} - P \frac{dV_R}{dt} + A_R \dot{Q}_{int} \tag{3-108}
\]

A discussion on the governing equations of a single stream transient CSTR has been presented in Tosun [211]. However, the cantera software assumes a multi-stream transient CSTR model. The derivation of the governing equations of the transient CSTR model has been discussed in section A.

### 3.2.4 Model Inputs

For each reservoir and reactor, a *mechanism file* had to be specified. These *Cantera mechanism (CTI) files* were equivalent to the *Chemkin* input files. However, a single *Cantera* mechanism file contains all the information for the reaction mechanism and species, while *Chemkin* requires individual files for the kinetic, thermodynamic and transport data.

The state variables, namely, pressure, temperature and composition were needed as user inputs for the reservoir states and reactor initial states. The mass flow rates for the MFRs and valve \( K_v \) values were provided determining the reactor pressure and stoichiometry. A linear valve response to pressure drop was used, as specified by default in Cantera combustion code. The value of \( K_v \) was set high enough so that the reactor pressure remains constant. For this study, a value of 0.5 was used for \( K_v \) for both valves.

The residence time was controlled by scaling the total inlet mass flow rate, which required an accurate estimate of the hot gas density. Hence, the simulations were repeated until agreement in predicted and actual residence times and densities was achieved.

The global vitiated combustion equation for biofuels was used to calculate mass flow rates for the inlet reactant streams. The reaction for \( \phi < 1 \) is given as:
\[(\phi) C_xH_yO_z + \left(x + \frac{y}{4} - \frac{z}{2}\right) [O_2 + (3.76) N_2] +
(\text{R}_n) \left[(\phi) (x) CO_2 + (\phi) \left(\frac{y}{2}\right) H_2O + (3.76) \left(x + \frac{y}{4} - \frac{z}{2}\right) N_2 + (1 - \phi) \left(x + \frac{y}{4} - \frac{z}{2}\right) O_2\right] \rightarrow
(1 + \text{R}_n) \left[(\phi) (x) CO_2 + (\phi) \left(\frac{y}{2}\right) H_2O + (3.76) \left(x + \frac{y}{4} - \frac{z}{2}\right) N_2 + (1 - \phi) \left(x + \frac{y}{4} - \frac{z}{2}\right) O_2\right]
\]

The exhaust gas recirculation (EGR) stream mass flow rate and temperature were also specified. The mass flow rate of the fuel inlet was given by equation 3–109. An igniter reservoir was added in order to artificially ignite a combustible fuel-air mixture. A short duration gaussian pulse of high temperature hydrogen atoms may be used for the purpose. The mass flow rate of igniter inlet is given by equation 3–110. However, for this study, the igniter mass flow rate was set to zero. The mass flow rate of air inlet was given by equation 3–111.

\[
\hat{m}_1 = \hat{m}_F = \phi \cdot \bar{M}_F \cdot \dot{n}_F
\]  

\[
\hat{m}_2 = \text{Gaussian} \left(t_0, A_I, \sigma_I\right)
\]  

\[
\hat{m}_3 = \hat{m}_A = 4.76 \cdot \bar{M}_A \left(x + \frac{y}{4} - \frac{z}{2}\right) \cdot \dot{n}_F = \alpha \cdot \hat{m}_1
\]

The mass-based recirculation ratio \(R_m\) (or EGR) was a specified parameter and was defined as the ratio of mass flow rate of the recirculation stream, to that of the fresh air stream. Hence, the mass flow rate of exhaust gas recirculation stream was calculated by equation 3–112. The total mass flow rate was calculated based on equation 3–113 as the sum of the mass flow rates of fuel, igniter, air and EGR streams. The igniter mass flow rate, is non-zero for only a short duration of time, to initiate combustion. The residence time was found using equation 3–114.
\[ \dot{m}_4 = \dot{m}_R = R_m \cdot \dot{m}_3 \]  
(3–112)

\[ \dot{m}_T = \dot{m}_1 + \dot{m}_2 + \dot{m}_3 + \dot{m}_4 \]  
(3–113)

\[ \tau_{\text{res}} = \frac{\rho V_R}{\dot{m}_T} \]  
(3–114)

The scaling of the mass flow rates in order to achieve the required residence time was achieved through the determination of \( \dot{n}_F \) given by equation 3–115, based on predicted hot gas density \( \rho \). The valve exit mass flow rate \( \dot{m}_{\text{valve}} \), was calculated using equation 3–116.

\[ \dot{n}_F = \frac{\rho V_R}{\tau_{\text{res}} \left( \phi \cdot M_F + 4.76 \cdot M_A (1 + R_m) \left( x + \frac{y}{4} - \frac{z}{2} \right) \right)} \]  
(3–115)

\[ \dot{m}_{\text{valve}} = K_v \cdot \Delta P_{\text{valve}} \]  
(3–116)

### 3.2.5 Performance Parameters

The combustion performance parameters were calculated based on equation 3–117 through equation 3–119. The emission index (EI) of a species is defined as the mass production rate of the species per unit mass flow rate of fuel \( [212] \), as given by equation 3–117, assuming that \( Y_{R,j} = Y_{ex,j} \). It may further be noted that the emission index, in our work was defined based on the net species outflow. For most pollutant species of interest, this difference may be a non-issue, since \( Y_{F,j} \) and \( Y_{A,j} \) may be safely assumed to be zero. However, for fuels like syngas and acetylene \( Y_{F,j} \) may not be zero for species like acetylene, \( H_2 \) and \( CO \), but we have disregarded these. The definition of efficiency as specified by equation 3–118, is based on the work of Zelina et al.\([109] \). The loading parameter is a measure of blowout stability and was calculated based on equation 3–119. The constant \( n \) had a value of 2. Further details about \( LP \) may be found in \([6, 106, 107, 109] \).
\[ EI_j = \frac{\dot{m}_T \cdot Y_{ex,j} - \dot{m}_F \cdot Y_{F,j} - \dot{m}_A \cdot Y_{A,j} - \dot{m}_R \cdot Y_{R,j}}{\dot{m}_F} \]  

\[ = \frac{\dot{m}_F (Y_{ex,j} - Y_{F,j}) + \dot{m}_A (Y_{ex,j} - Y_{A,j})}{\dot{m}_F} \]  

\[ \eta_e = 1 - \left[ \frac{EI_{UHC} + 0.232EI_{CO}}{1000} \right] \]  

\[ LP = \frac{\dot{V}_T}{V_R P_n} \]

### 3.3 Modeling Approach

The actual gas turbine emissions, efficiency and stability involve a complex interplay of several factors like physical properties of fuel, such as ignition delay, cetane number, viscosity and the combustion system design itself. These may further affect the atomization quality, evaporation rate, etc. and ultimately, the combustion parameters of our interest. We have attempted to look at the combustion performance from the point of view of pure chemical kinetics, isolating the interaction effects of the parameters observed in a physical system. The primary zone of the combustor was modeled as a constant pressure CSTR, with a constant supply of the inlet charge from fuel, air and EGR streams, at predetermined rates and states. The air stream temperature \( T_A \) and EGR temperature (EGRT) were always set equal (unless explicitly specified), while fuel stream temperature \( T_F \) was fixed at 300 K. The model assumes instantaneous mixing and spatial homogeneity of gas mixture inside the CSTR. The simplicity of the model yields an intuitive understanding of the processes affecting combustion performance. The C++ interface of Cantera \([210]\) combustion code was used for modeling. The combustion performance of various biofuels namely, ethanol, dimethyl ether and methyl butanoate which is a biodiesel surrogate has been compared against that of n-heptane, which is a surrogate for diesel. In a separate study, the combustion performance of syngas...
was compared to that of methane. The mechanisms used for ethanol, dimethyl ether, methyl butanoate and n-heptane were taken from the Lawrence Livermore National Laboratory (LLNL) website [213]. Further studies on blowout stability were performed for stoichiometric combustion of ethanol and varying EGR levels and EGR temperatures. For the study of soot formation, acetylene fuel was chosen, since its chemistry is fairly well known. The mechanism developed by Frenklach and coworkers was used for syngas, methane and acetylene fuels. Table 3-1 summarizes the mechanisms used to model the combustion kinetics for each of the fuels.

In this study, combustion blowout stability has been assumed to be resulting from kinetic processes, and measured in terms of the loading parameter (LP) given by equation 3–119. Combustion stability is defined as the measure of resistance to a flame blowout condition, which occurs when the heat release rate from the reaction is insufficient to raise the temperature of the reactants to the steady state reaction temperature. As a result, a sustained high temperature flame is not attainable, and the CSTR exit state eventually becomes identical to the inlet reactant state. The term combustion stability, as used in this work should not be confused with that used in the context of pressure fluctuations and unsteady heat release, as experienced in an unsteady combustion process. The total inlet mass flow rate at a fixed equivalence ratio and EGR was increased until the flame temperature dropped to that of the mixed unreacted inlet stream, indicating absence of a reaction. The maximum mass flow rate at which a steady state flame condition was achieved, was treated as the blowout limit for a given equivalence ratio and EGR level. Specific constraints applied to individual case studies have been discussed in sections 3.3.1 through 3.3.7.

The applicability of the model is generally limited to reasonably low pressures, since at higher pressures, the blowout stability may not be kinetically controlled and soot formation at higher pressures may be significantly influenced by fractal aggregation effects.
3.3.1 Case Study 1: Syngas and Methane Fuel Simulations

The combustor pressure and volume were fixed at 202.65 kPa (2.0 atm) and 250e-6 m³ (0.25 Liter), respectively. The combustor was initialized to a temperature of 2000 K and the composition was set to the major product species of combustion, to simulate a steady flame with a temperature above the auto-ignition temperature of the inlet reactants. The emissions (at residence time of 5.0 ms) and blowout limits for three different mixtures of syngas were compared, namely, Syn75 (CO: 0.25, H₂: 0.75), Syn50 (CO: 0.5, H₂: 0.5) and Syn25 (CO: 0.75, H₂: 0.25). Simulations were performed for each of these fuel compositions over the equivalence ratios ranging from 0.4 to 3.0, and three different levels of EGR with adiabatic recirculation at recirculation ratios of 0.0, 1.0 and 2.0. In a subsequent part of this work, three levels of non-adiabatic EGR with a recirculation temperature of 1200 K were tested. The air stream temperature (T_A) was maintained constant at 400 K. The constant residence time simulations were run for 5.0 ms.

3.3.2 Case Study 2: Biofuels and n-Heptane Fuel Simulations

The combustion performance of various biofuels namely, ethanol, dimethyl ether and methyl butanoate which is a biodiesel surrogate has been compared against that of n-heptane, which is a surrogate for diesel. In the first set of runs, the blowout performance of the fuels has been investigated, for equivalence ratios varying from 0.4 to 1.0 at intervals of 0.1, and EGR levels of 0.0, 1.0 and 2.0. The EGR stream was cooled to a temperature of 700 K, and the combustor pressure and volume were fixed at 202.65 kPa (2.0 atm) and 0.00258 m³ (15.71 in³), respectively. The combustor state was initialized to a constant CSTR pressure of 202.65 Pa (2 atm), a temperature of 2000 K and the composition was set to the major product species of combustion, to simulate a steady flame with a temperature above the auto-ignition temperature of the inlet reactants. For simulations at fixed residence time, the value of 10.0 ms was used.
3.3.3 Case Study 3: Study of EGR Temperature/EGR level on Ethanol Blowout Limits

The blowout performance of ethanol fuel was tested for equivalence ratio of 1.0 and EGR temperatures ranging from 400 to 1200 K at intervals of 200 K. Comparison of these runs has been presented for EGR levels of 0.0, 0.5, 1.0, 1.5 and 2.0. The combustor pressure and volume were held fixed at 202.65 kPa (2 atm) and 0.00258 m$^3$ (15.71 in$^3$), respectively. The blowout stability was quantified in terms of LP given by equation 3–119. The effect of reduction in loading parameter as a function of EGR and EGR temperature have been plotted. The results were normalized to the corresponding values for the open cycle (EGR=0.0) case. The effect of pressure was also investigated, by varying the pressures from 0.5 to 2.0 atm, in steps of 0.5 atm.

In a subsequent study, ignition delays were calculated for stoichiometric combustion of ethanol in a constant pressure batch reactor, at varying EGR levels and reactant inlet temperatures. The ignition delay was further used for estimation of the ignition number. Further, correlations of variations of LP with OH emission indices have been presented.

3.3.4 Case Study 4: A Study of the Effect of EGR Temperature/EGR level/Residence Time/Equivalence Ratio on Soot Formation (Acetylene Fuel Combustion)

The soot formation process was modeled using detailed chemical kinetic mechanism for soot formation by Frenklach and coworkers (Appel et al. [148]). For this study, particulate growth model for soot formation was omitted and only detailed kinetic model was used to study the processes involved in gas phase chemistry leading to soot nucleation. The effect of EGR, EGR temperature, equivalence ratio and residence time on soot formation was investigated. The combustor pressure and volume were held fixed at 202.65 kPa (2 atm) and 0.00258 m$^3$ (15.71 in$^3$), respectively. The following cases were analyzed:

1. case 1: EGR = 0.0-5.0, φ = 2.0, $\tau_{res}$ = 1.0, EGRT=1000 K
2. case 2: EGRT = 400-1200 K, EGR = 0.0 and 2.0, φ = 2.0, $\tau_{res}$ = 1.0
3. case 3: φ = 0.5-5.0, EGR = 0.0 and 2.0, $\tau_{res}$ = 1.0, EGRT=1000 K
4. case 4: $\tau_{res} = 0.1$-10.0, $\phi = 2.0$, EGR = 0.0 and 2.0, EGRT=1000 K

3.3.5 Case Study 5: Soot Particle Growth and Oxidation in Vitiated Combustion of Acetylene Fuel

The soot formation dynamics was simulated in a CSTR network model, with modifications to the Cantera CSTR model to include the kinetic coupling of heterogeneous soot growth processes, using the method of moments. The method of moments approach for particulate soot modeling, and the detailed chemistry of soot formation used, was based on the work by Frenklach and coworkers [148–150, 158, 171, 187–190, 192–194, 196–201]. The detailed chemical kinetic mechanism is based on [148]. The fortran code with the comprehensive particulate model used [149, 208] included submodels for surface chemistry [148], nucleation [150], and coagulation [149, 188, 189]. The conservation equations in Cantera zero-dimensional reactor were modified to include the correction terms from the soot code. An interfacing class written in C++, allowed simultaneous calculations of the soot aerosol dynamics problem from the fortran soot code (using an extern call) and the native C++ zero-dimensional reactor class. The model validation was performed against the results from Brown et al. [159] using detailed chemistry from Wang and Frenklach [195], particulate model from Revzan et al. [208] and surface chemistry submodel from Kazakov et al. [158]. In order to obtain an understanding of the uncertainties in the predictions, the results from this model were compared to the soot formation model developed by Richter et al. [183], Ergut et al. [184], Richter et al. [214]. Their model used the sectioning approach, in which the chemistry of 20 discrete soot particle bins was modeled. The bins with a suffix “J”, indicated radical bins. The first few bins were treated as soot precursors, while bins beyond bin4 were treated as soot particles. The advantage of the sectioning approach was that the bins could be treated as individual species, and the chemistry could be integrated with the gas phase mechanism. The thermodynamic parameters for the bins were not specified; instead the forward and reverse reactions were independently specified.
The conditions of simulation were $\phi=2.0$, $P = 202.65$ kPa (2 atm), EGR = 0.0 and 2.0. The simulations were run at a residence time ($\tau_{\text{res}}$) of 1.0 ms with specified flame temperatures between 1500-2000 K. The soot volume fraction, average soot diameter, soot surface area, soot particle mass density, and smoke number were modeled. The simulations were performed under similar conditions for Richter soot mechanism. The bin and the radical bin mass fractions (beyond bin 4) were used to determine the soot volume fractions. The smoke number (SN) was modeled using correlations developed by Colket III et al. [141].

3.3.6 Case Study 6: Modeling of Semi-Closed Cycle Engine Characteristics using a Kinetically Equivalent Unvitiated Open-Cycle CSTR System

The focus of this study was to demonstrate the use of an approach to model a semi-closed cycle (SCC) engine using a kinetically equivalent unvitiated open cycle (OC) model. This approach has the advantage of being able to reproduce characteristic curves of a more complex system using a simpler model, and allows the use of available data in the literature on OC engines for equivalent SCC engines. This approach is of significance in reducing the need for further experimentation on semiclosed cycles. The steady state CSTR conditions for both OC and SCC cases were compared, to determine the “matching conditions” for the two models. The temperature suppression effect of vitiation in SCC CSTR, was modeled by an equivalent lower inlet air temperature (cases A and B) entering an adiabatic OC CSTR, or a heat loss term (cases C and D) in a non-adiabatic CSTR. The residence time effect has been modeled using appropriate mass flow scaling calculations. A set of numerical simulations with the equivalent CSTR network models were performed, to validate the results of the theoretical analysis.

The matching conditions for a kinetically equivalent OC, are based on a match in the exit enthalpies and species production rates. Four equivalent systems were analyzed:

**Case A:** An adiabatic OC system equivalent to an SCC system, with lower reactant inlet temperatures and larger residence time with matched fresh reactant flows.
**Case B:** An adiabatic OC system equivalent to an SCC system, with lower reactant inlet temperatures and matched residence time.

**Case C:** A non-adiabatic OC system equivalent to an SCC system, with a positive heat loss and larger residence time with matched fresh reactant flows.

**Case D:** A non-adiabatic OC system equivalent to an SCC system, with a positive heat loss and matched residence time.

---

In the preliminary test simulations, it was found that the modeling based on equivalent lower inlet air temperature, was severely constrained by the lowest air temperature (300 K) that could reliably be used. On the other hand, the use of a heat flux term to model
flame temperature suppression, had no such constraint. The mass flow scaling based on matching the residence time of fresh reactants (cases A and C in section 4.7.3) was found to be less complicated an approach than the matching of the residence time based on the total mass flow. Therefore, the use of an equivalent OC system for predicting the chemical kinetic trends of a SCC system was demonstrated, based on the approach in case C. Simulations were run for $\phi = 1.0$, and $\tau_{res} = 10$ ms (for SCC system), EGRT = 600, 800, 1000 and 1200 K, EGR = 0.0 and 2.0. For an SCC system with these conditions, an equivalent OC system was modeled using the mass flow scaling based on case 3 section 4.7.3. An appropriate heat loss term was calculated to match the exit temperatures for the SCC and the OC systems. The plots of flame temperature and emission indices for unburned hydrocarbons (UHC), CO and OH were plotted.

### 3.3.7 Case Study 7: A Sensitivity Analysis Study on Combustion Performance of Ethanol Fuel Close to Blowout

A sensitivity analysis study was carried out for ethanol fuel close to blowout. The simulation conditions were $\phi = 1.0$, EGRT = 1000 K, and EGR = 0.0, 2.0. The relative and absolute tolerances for the sensitivity solution were 0.005. The key assumption behind this analysis is that the sensitivity of the blowout limit is a strong function of the OH concentration sensitivity. The most influential reactions affecting the OH concentrations were identified.

![Figure 3-8. Semi-Closed Cycle CSTR Network Model](image)
Figure 3-9. Model Inputs

Table 3-1. Combustion mechanisms

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Species</th>
<th>Reactions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>57</td>
<td>383</td>
<td>Marinov [136]</td>
</tr>
<tr>
<td>DME</td>
<td>79</td>
<td>660</td>
<td>Fischer et al. [215]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Curran et al. [216]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Kaiser et al. [217]</td>
</tr>
<tr>
<td>MB</td>
<td>264</td>
<td>1966</td>
<td>Fisher et al. [218]</td>
</tr>
<tr>
<td>n-Heptane (reduced)</td>
<td>160</td>
<td>1540</td>
<td>Seiser et al. [219]</td>
</tr>
<tr>
<td>Methane</td>
<td>101</td>
<td>544</td>
<td>Appel et al. [148, 220]</td>
</tr>
<tr>
<td>Syngas</td>
<td>101</td>
<td>544</td>
<td>Appel et al. [148, 220]</td>
</tr>
<tr>
<td>Acetylene</td>
<td>101</td>
<td>544</td>
<td>Appel et al. [148, 220]</td>
</tr>
<tr>
<td>Acetylene</td>
<td>296</td>
<td>6663</td>
<td>Richter et al. [183, 214], Ergut et al. [184]</td>
</tr>
</tbody>
</table>
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Case Study 1: Syngas and Methane Fuel Simulations

4.1.1 Effect of Fuel Composition and Equivalence Ratio at EGR=0

The impact of variability in fuel composition on combustion performance was studied for a range of equivalence ratios from 0.4 to 3.0. Figure 4-1 depicts the variation in steady state continuously stirred tank reactor (CSTR) temperature as a function of equivalence ratio for Methane and three compositions of syngas tested, Syn75 (CO: 0.25, H₂: 0.75), Syn50 (CO: 0.5, H₂: 0.5) and Syn25 (CO: 0.75, H₂: 0.25). The maximum temperature was found to occur under fuel-rich conditions for syngas mixtures and was near stoichiometric conditions for Methane, for the range of conditions tested. The combustion of syngas mixtures produced higher flame temperatures as compared with Methane fuel. Hence, NOₓ production rates could be higher for syngas. However, operating these fuels in a semiclosed cycle (SCC), which has the effect of lowering flame temperatures, is likely to considerably mitigate this effect.

The combustion efficiency and loading parameter for the system, were calculated as described in Zelina and Ballal [109]. The combustion efficiency was found to drop steadily for syngas mixtures with rising equivalence ratios, as shown in Figure 4-2. The Syn25 mixture had generally higher efficiencies over most equivalence ratios as compared to the other two mixtures, Syn75 being the lowest amongst syngas mixtures. The combustion efficiency of Methane was significantly lower, especially on the fuel-rich side.

The emission index for CO increased by about a factor of 2 between equivalence ratios of 0.4 to 3.0, as can be seen in Figure 4-3. Under lean conditions, Methane produced highest emission index (EI) for CO and for syngas mixtures, Syn25 was found to produce the maximum EI CO, followed by Syn50 and Syn75, Syn75 being the lowest. At equivalence ratios between 1 to 2, CO emissions for Methane were considerably higher than syngas. The plots for EI UHC versus equivalence ratio are shown in Figure 4-4.
Syn75 syngas mixture had UHC emissions comparable to Methane on the fuel-lean side, while much lower EI UHC on the fuel-rich side. The UHC emissions for Syn25 were found to be lowest, while Syn75 had highest EI UHC next to Methane. The UHC emissions for Methane were about an order of magnitude higher than any of the syngas mixtures on the fuel-rich side.

Figure 4-5 depicts the EI UHC versus combustion efficiency trends. The UHC emissions changed by about an order of magnitude with a change in efficiency from over 0.99 to below 0.70, depending on the fuel. The plot shows that UHC emissions may decrease despite a reduction in efficiency, indicating a possible increase in CO emissions corresponding to the efficiency loss.

Figure 4-1. Comparison of flame temperatures for fuels Methane, Syn75, Syn50 and Syn25 as a function of equivalence ratio at EGR = 0.0, \( \tau_{res} = 5.0 \) ms, \( P = 202.65 \) kPa (2 atm), \( T_A = 400 \) K.

The dependence of combustion efficiency on steady state combustion flame temperatures has been presented in Figure 4-6. The lean-side data resulted in higher efficiencies as expected. The efficiencies were maximum for Syn25, followed by Syn50 and Syn75, in that order. A drastic fall-off of efficiency was observed for Methane mixture, while the efficiency of all syngas mixtures was higher than 0.7, for equivalence ratios between 0.4 and 3.
Figure 4-2. Comparison of combustion efficiency for fuels Methane, Syn75, Syn50 and Syn25 as a function of equivalence ratio at EGR = 0.0, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.

Figure 4-3. Comparison of CO emission index for fuels Methane, Syn75, Syn50 and Syn25 as a function of equivalence ratio at EGR = 0.0, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.
Figure 4-4. Comparison of UHC emission index for fuels Methane, Syn75, Syn50 and Syn25 as a function of equivalence ratio at EGR = 0.0, $\tau_{res} = 5.0$ ms, P = 202.65 kPa (2 atm), $T_A = 400$ K.

Figure 4-5. Variation of UHC emission index for fuels Methane, Syn75, Syn50 and Syn25 as a function of combustion efficiency at EGR = 0.0, $\tau_{res} = 5.0$ ms, P = 202.65 kPa (2 atm), $\phi = 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0$ (fuel-lean side) and $\phi = 1.2, 1.6, 2.0, 3.0$ (fuel-rich side), $T_A = 400$ K.
Figure 4-6. Variation of combustion efficiency for fuels Methane, Syn75, Syn50 and Syn25 as a function of flame temperature at EGR = 0.0, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K, $\phi = 0.4, 0.6, 0.8, 1.0$ (fuel-lean side) and $\phi = 1.2, 1.6, 2.0, 3.0$ (fuel-rich side).
4.1.2 Effect of Adiabatic Exhaust Gas Recirculation (EGR)

The effect of EGR under conditions of adiabatic recirculation on the combustion efficiency was studied. Under these conditions, the inlet recirculation stream (Stream 4 in Figure 3-8) into the combustor has nearly the same temperature as the combustor exit temperature. The only difference in temperatures would arise from the fact that the combustor exhaust was still allowed to react in the Flow Split reactor for a small finite residence time. Figure 4-7 depicts the temperature-efficiency dependence for syngas mixtures for EGR of 0.0 and 2.0, respectively. The model results have been plotted at equivalence ratios of 0.4, 0.6, 0.8, 1.0, 1.2, 1.6, 2.0 and 3.0. The flame temperatures and efficiency increased with increasing EGR to 2.0. There is a significant drop in rich-side efficiency of all syngas mixtures at EGR of 2.0. Syn3 had the lowest efficiency on the rich-side while Syn2 had the highest, at almost all equivalence ratios, for the EGR levels tested. Moreover, the effect of variations in compositions of the mixtures was more pronounced on the fuel-rich side of the temperature-efficiency loop.

![Figure 4-7](image)

(a) EGR=0.0

(b) EGR=2.0

Figure 4-7. Variation of combustion efficiency for fuels Syn75, Syn50 and Syn25 as a function of flame temperature at EGR = 0.0 and 2.0, $\tau_{res} = 5.0$ ms, P = 202.65 kPa (2 atm), $T_A = 400$ K.

The effect of adiabatic EGR on the combustion performance of the three fuels was tested for three different equivalence ratios. Figures 4-8 to 4-11 depict the effect of EGR at $\phi = 0.4$. Figures 4-12 to 4-15 were plotted for $\phi = 1.0$ while Figures 4-16 to 4-19
correspond to $\phi = 1.6$. Figure 4-8 shows the effect of adiabatic EGR on temperature. The combustor flame temperatures increased with increase in adiabatic EGR. The effect of composition variances on temperature was found to increase with increasing levels of EGR at $\phi = 0.4$. The effect of EGR on combustion efficiency is shown in 4-9. At $\phi = 0.4$, the combustion efficiencies for Syn25 were found to be maximum over all levels of EGR tested, while those for Syn75 were lowest. With rising levels of EGR, the difference in combustion efficiencies of the three compositions was also found to increase, while all the mixtures showed a general upward trend in efficiency at $\phi = 0.4$.

![Figure 4-8](image)

Figure 4-8. Variation of flame temperature for fuels Syn75, Syn50 and Syn25 as a function of adiabatic EGR at $\phi = 0.4$, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.

The effect of EGR (at $\phi = 0.4$) on EI UHC and EI CO, can be seen in Figures 4-10 and 4-11, respectively. The EI UHC was maximum for Syn75 while EI CO was maximum for Sun 25 for all EGR. The UHC and CO emissions were relatively low for all mixtures and decreased with EGR. At $\phi = 1.0$, the flame temperatures and combustion efficiency increased, while emission indices of CO and UHC decreased with adiabatic EGR. The Syn75 mixture had the maximum temperature while Syn25 had the lowest. As can be seen in Figures 4-12 to 4-15, the effect of composition variability on CO emissions, temperature and efficiency reduced slightly at $\phi = 1.0$, with increasing EGR. At $\phi = 1.6$, wider differences in parameters could be observed, as depicted by Figures 4-16 to 4-19. All
mixtures showed an increase in temperature with adiabatic EGR, that for Syn25 being maximum. With increasing EGR, all mixtures showed small increases in efficiency and a slight reduction in EI CO and UHC.

Figure 4-9. Variation of combustion efficiency for fuels Syn75, Syn50 and Syn25 as a function of adiabatic EGR at $\phi = 0.4$, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.

Figure 4-10. Variation of UHC emission index for fuels Syn75, Syn50 and Syn25 as a function of adiabatic EGR at $\phi = 0.4$, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.
Figure 4-11. Variation of CO emission index for fuels Syn75, Syn50 and Syn25 as a function of adiabatic EGR at $\phi = 0.4$, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.

Figure 4-12. Variation of flame temperature for fuels Syn75, Syn50 and Syn25 as a function of adiabatic EGR at $\phi = 1.0$, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.
Figure 4-13. Variation of combustion efficiency for fuels Syn75, Syn50 and Syn25 as a function of adiabatic EGR at $\phi = 1.0$, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.

Figure 4-14. Variation of UHC emission index for fuels Syn75, Syn50 and Syn25 as a function of adiabatic EGR at $\phi = 1.0$, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.
$\phi=1.0$, $\tau_{res}=5.0$ ms, $P=202.65$ kPa (2 atm), $T_A=400$ K.

Figure 4-15. Variation of CO emission index for fuels Syn75, Syn50 and Syn25 as a function of adiabatic EGR at $\phi = 1.0$, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.

$T_A=400$ K

Figure 4-16. Variation of flame temperature for fuels Syn75, Syn50 and Syn25 as a function of adiabatic EGR at $\phi = 1.6$, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.
Figure 4-17. Variation of flame temperature for fuels Syn75, Syn50 and Syn25 as a function of adiabatic EGR at $\phi = 1.6$, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.

Figure 4-18. Variation of UHC emission index for fuels Syn75, Syn50 and Syn25 as a function of adiabatic EGR at $\phi = 1.6$, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.
Figure 4-19. Variation of CO emission index for fuels Syn75, Syn50 and Syn25 as a function of adiabatic EGR at $\phi = 1.6$, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.
4.1.3 Effect of Non-Adiabatic Exhaust Gas Recirculation

At the flow split reactor, a wall with a specified overall heat transfer coefficient was added to control the EGR inlet temperature for Stream 4 to a specified value of 1200 K. The target EGR inlet temperatures for Stream 4 were achieved by setting arbitrarily high heat flux values by assigning very high values of the overall heat transfer coefficient, wall surface area and the temperature of the cold-side fluid to 1200 K. The effect of non-adiabatic EGR with an inlet temperature of 1200 K has been studied, and the results have been presented in figures 4-20 through 4-26 for Syn25 fuel. Clearly, as can be observed from figure 4-20, with increasing EGR, there was a drop in combustion temperature at all equivalence ratios. Figure 4-21 shows a plot of combustion efficiency versus equivalence ratio. Increasing EGR reduced CO and UHC emission indices slightly while increased combustion efficiency, as shown in Figures 4-22 and 4-23. Depending on the EGR level, a CO emissions minimum emerges at an equivalence ratio of about 0.6.

![Figure 4-20](image)

*Figure 4-20. Comparison of flame temperature for Syn25 fuel with EGR of 0.0, 0.2 and 0.5 as a function of equivalence ratio at EGRT = 1200 K, \( \tau_{res} = 5.0 \) ms, \( P = 202.65 \) kPa (2 atm), \( T_A = 400 \) K.*
Figure 4-21. Comparison of combustion efficiency for Syn25 fuel with EGR of 0.0, 0.2 and 0.5 as a function of equivalence ratio at EGRT = 1200 K, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.

Figure 4-22. Comparison of CO emission index for Syn25 fuel with EGR of 0.0, 0.2 and 0.5 as a function of equivalence ratio at EGRT = 1200 K, $\tau_{res} = 5.0$ ms, $P = 202.65$ kPa (2 atm), $T_A = 400$ K.
Figure 4-23. Comparison of UHC emission index for Syn25 fuel with EGR of 0.0, 0.2 and 0.5 as a function of equivalence ratio at \( \text{EGR} = 1200 \text{ K}, \tau_{\text{res}} = 5.0 \text{ ms}, P = 202.65 \text{ kPa (2 atm)}, T_A = 400 \text{ K}. \)

Figure 4-24. Comparison of UHC emission index for Syn25 fuel with EGR of 0.0, 0.2 and 0.5 as a function of combustion efficiency at \( \text{EGR} = 1200 \text{ K}, \tau_{\text{res}} = 5.0 \text{ ms}, P = 202.65 \text{ kPa (2 atm)}, T_A = 400 \text{ K}, \phi = 0.4, 0.6, 0.8, 1.0 \) (fuel-lean side) and \( \phi = 1.2, 1.6, 2.0, 3.0 \) (fuel-rich side).
Figure 4-25. Comparison of combustion efficiency for Syn25 fuel with EGR of 0.0, 0.2 and 0.5 as a function of flame temperature at \( \text{EGR} = 1200 \text{ K}, \tau_{\text{res}} = 5.0 \text{ ms}, P = 202.65 \text{ kPa (2 atm)}, T_A = 400 \text{ K}, \phi = 0.4, 0.6, 0.8, 1.0 \) (fuel-lean side) and \( \phi=1.2, 1.6, 2.0, 3.0 \) (fuel-rich side).

Figure 4-26. Variation of CO emission index for Syn25 fuel with EGR of 0.0, 0.2 and 0.5 as a function of combustion efficiency at \( \text{EGR} = 1200 \text{ K}, \tau_{\text{res}} = 5.0 \text{ ms}, P = 202.65 \text{ kPa (2 atm)}, T_A = 400 \text{ K}, \phi = 0.4, 0.6, 0.8, 1.0 \) (fuel-lean side) and \( \phi=1.2, 1.6, 2.0, 3.0 \) (fuel-rich side).
4.1.4 Effect of Fuel Composition and EGR on Extinction Limits

The lean-side extinction limits of syngas mixtures Syn50, Syn25 and Methane were also analyzed at adiabatic EGR of 0.0 and 2.0. Figures 4-27 and 4-28 show the plots of blowout equivalence ratios with loading parameter and residence time, respectively. The combustion stability was found to increase dramatically at an adiabatic EGR of 2. Syn50 showed the best blowout performance, followed by Syn25 and then Methane. This is not unexpected and may be attributed to higher H$_2$ content in Syn50, which exhibits much wider flammability limits than other hydrocarbon fuels.

![Figure 4-27. Variation of blowout equivalence ratio for Methane fuel with EGR = 0.0, Methane fuel with EGR = 2.0 (adiabatic), Syn50 fuel with EGR=0.0, Syn50 fuel with EGR=2.0 (adiabatic) and Syn25 fuel with EGR = 0.0 as a function of blowout loading parameter (LP) at P = 202.65 kPa (2 atm), T$_A$ = 400 K.](image)

In Figure 4-29, the effects of adiabatic and non-adiabatic EGR on combustion stability have been compared. It was found that, while the extinction limits were improved with adiabatic EGR, at an EGR stream temperature of 1200 K, a decrease in combustion stability was observed with rising levels of recirculation. Since, the increase in adiabatic EGR was accompanied by a corresponding decrease in inlet mass flow, for any given
residence time, the net effect of increasing adiabatic EGR was that of equivalently increasing the volume of the reactor, allowing more time for the fresh reactants to react. A nearly linear relationship was observed between the blowout equivalence ratio and reactor flame temperature for different conditions of EGR, and is depicted in Figure 4-30. It can be observed that the blowout temperatures were lower, with increasing EGR. Hence, it is important to note that in terms of temperature, the stability of SCC engines was improved with EGR. In Figure 4-31, the mixture inlet temperatures for Methane fuel, have been plotted for various equivalence ratios and EGR. It can be seen clearly, that the inlet mixture temperature increased with increasing EGR and with temperature of EGR stream. This has an effect of offsetting the impact of reduction in combustion stability due to dilution of the inlet stream.

![Graph showing variation of blowout equivalence ratio for Methane fuel with EGR = 0.0, Methane fuel with EGR = 2.0 (adiabatic), Syn50 fuel with EGR=0.0, Syn50 fuel with EGR = 2.0 (adiabatic) and Syn25 fuel with EGR = 0.0 as a function of blowout residence time at P = 202.65 kPa (2 atm), T_A = 400 K.](image)

Figure 4-28. Variation of blowout equivalence ratio for Methane fuel with EGR = 0.0, Methane fuel with EGR = 2.0 (adiabatic), Syn50 fuel with EGR=0.0, Syn50 fuel with EGR = 2.0 (adiabatic) and Syn25 fuel with EGR = 0.0 as a function of blowout residence time at P = 202.65 kPa (2 atm), T_A = 400 K.
Figure 4-29. Variation of blowout equivalence ratio for Methane fuel for EGR = 0.0, EGR = 0.2 (EGRT=1200K), EGR = 0.5 (EGRT=1200K) and EGR = 2.0 (adiabatic) as a function of blowout LP at P = 202.65 kPa (2 atm), $T_A = 400$ K.

Figure 4-30. Variation of blowout flame temperature for Methane fuel for EGR = 0.0, EGR = 0.2 (EGRT = 1200K), EGR = 0.5 (EGRT=1200K) and EGR = 2.0 (adiabatic) as a function of blowout equivalence ratio at $P = 202.65$ kPa (2 atm), $T_A = 400$ K.
Figure 4-31. Variation of reactant mixture inlet temperature for Methane fuel for EGR = 0.0, EGR = 0.2 (EGRT = 1200 K), EGR = 0.5 (EGRT = 1200 K) and EGR = 2.0 (adiabatic), $T_A$ = 400 K, $P$ = 202.65 kPa (2 atm) as a function of blowout equivalence ratio.
4.1.5 Effect of Fuel Composition and EGR on Soot Precursor Formation

The soot concentrations were quantified by the concentration of the soot precursors, the pyrene molecules ($A_4$ species). As depicted in Figure 4-32, the EI $A_4$ values observed were zero for all conditions tested for syngas fuels. With Methane fuel, EI $A_4$ values were observed only at fuel-rich equivalence ratios greater than 1.6. It was observed that the $A_4$ emissions increased with increase in adiabatic EGR at high equivalence ratios. Further investigations with fuels with higher sooting tendency, is required, to be able to draw firm conclusions from the analysis. We believe, that the low sooting limits may purely be the result of homogeneity of combustion, assumed for a CSTR model, and may not be representative of the environment inside the combustor of a practical gas turbine combustor.

Figure 4-32. Variation of pyrene emission index for Methane fuel with EGR=0.0, EGR = 1.0 (adiabatic) and EGR = 2.0 (adiabatic) as a function of blowout equivalence ratio at $P = 202.65$ kPa (2 atm).
4.2 Case Study 2: Biofuels and n-Heptane Fuel Simulations

A comparison of the combustion blowout predictions for the biofuels is presented in Fig. 4-33 through Fig. 4-38. For the sake of clarity, only cases for EGR of 0.0 (solid markers) and EGR of 2.0 (hollow markers) have been depicted. The blowout temperatures were found to drop with decreasing equivalence ratios for all fuels. Additionally, since the simulations close to blowout limit were inherently unstable, some dispersion about the trendlines is not unexpected. We found that numerical instabilities were significant close to flame blowout, especially at high recirculation ratios. In some cases, solution multiplicities were noticed such that, for the same initial conditions, both flameout and steady flame solutions were obtained. Combustion could be sustained at lower temperatures with increasing EGR, hence lower blowout temperatures were observed for higher EGR, as seen in Fig. 4-33. Interestingly, at an EGR of 2.0, the gap between the blowout (BO) temperatures of all fuels grew narrower, supporting the fact that the Power, Water Extraction and Refrigeration (PoWER) system was less sensitive to variabilities in fuel composition.

As shown in Fig. 4-34 and Fig. 4-35, high CO and UHC emissions were observed for all fuels just before blowout. Since we would expect the combustion efficiency to be very low around blowout, these plots show the upper limits of CO and UHC emissions and depict the relative pollutant generation tendencies for each of the fuels. Maximum CO emissions at blowout were produced by n-heptane followed by Methyl Butanoate (MB), ethanol and lastly Dimethyl Ether (DME) at an EGR of 0.0. At the EGR of 2.0, much lower EI CO values were observed, and the difference in EI CO of different fuels was much less. Minimum EI CO and EI UHC values were observed at equivalence ratios of about 0.7 for most fuels. At an EGR of zero, n-heptane had the highest EI UHC while all biofuels produced roughly similar EI UHC values. It was found that EGR significantly reduced the EI UHC and EI CO, in part due to reduction of the exit mass flow rate ($\dot{m}_T - \dot{m}_R$) as a result of EGR.
Figure 4-33. Comparison of blowout flame temperature as a function of blowout equivalence ratio for Ethanol, DME, MB, n-Heptane fuels at EGR = 0.0 and 2.0, $T_A = \text{EGRT} = 700 \text{ K}$, $P = 202.65 \text{ kPa (2 atm)}$.

Figure 4-36, shows the plot of blowout equivalence ratio versus loading parameter. The maximum combustion blowout stability did not always occur at BO equivalence ratios of 1. This result was unexpected since with equivalence ratios approaching 1.0, the flame temperatures would be higher, which should enhance combustion stability. At EGR of 0.0, the combustion stability of MB was highest, followed by n-heptane, DME and ethanol being the least stable. However, at EGR of 2.0, ethanol had maximum BO stability followed by MB and then n-heptane and DME. Hence, the application of MB and ethanol blends may be advantageous in PoWER system in improving stability, in addition to enhancing the ignition performance as a result of increased volatility, as suggested by Bolszo et al. [126]. However, there was a significant drop in stability with increasing EGR for all fuels. Clearly, lower BO equivalence ratios were possible even at much higher
Figure 4-34. Comparison of blowout CO emission index as a function of blowout equivalence ratio for Ethanol, DME, MB, n-Heptane fuels at EGR = 0.0 and 2.0, $T_A = EGR T = 700$ K, $P = 202.65$ kPa (2 atm).

Loading parameters for EGR of 0.0 in comparison to the case with EGR of 2.0. This highlights an inherent drawback of reduced combustion stability in the PoWER system. This drawback may be overcome by the use of fuels with wider blowout stability limits like hydrogen or syngas, use of higher recirculation temperatures wherever applicable, or possibly techniques like $H_2$ enrichment.

Fig 4-37 depicts the plot of BO equivalence ratio as a function of residence time, while Fig. 4-38 depicts BO equivalence ratio versus total mass flow rate. The limiting residence times for EGR of 0.0 were almost an order of 2.0 lower than those for EGR of 2.0.

The Figures 4-39 through 4-44 were plotted at a residence time of 10 ms. Figure 4-39 shows plot of equivalence ratio versus temperature. There is a marked reduction in flame temperature with increase in EGR, for all fuels. With increasing EGR, the difference in flame temperatures for different fuels decreases. DME produced maximum flame temperature for all equivalence ratios, followed by n-heptane, MB and the lowest
Figure 4-35. Comparison of blowout UHC emission index as a function of blowout equivalence ratio for Ethanol, DME, MB, n-Heptane fuels at EGR = 0.0 and 2.0, $T_A = \text{EGRT} = 700$ K, $P = 202.65$ kPa (2 atm).

being that of ethanol. Combustion efficiency versus equivalence ratio has been plotted in Fig. 4-40. MB and DME had higher or comparable efficiencies, followed by ethanol and then n-heptane over most equivalence ratios. For the case of zero EGR, the combustion efficiency increased with decreasing equivalence ratio, for the equivalence ratios between 0.4 to 1.0. With an increase in EGR, the combustion efficiency increased and an optimum equivalence ratio emerged for maximum efficiency. Moreover, the optimum equivalence ratio shifted right towards stoichiometric, with increase in EGR.

Figures 4-41 and 4-42 show plots of equivalence ratio versus EI CO and EI UHC respectively. The CO emissions were highest for n-heptane while the other fuels showed nearly the same tendency to CO formation, for EGR of 0.0 as well as 2.0. For an EGR of 0.0 and 2.0 the lowest emissions were observed around an equivalence ratios of about 0.5 and 0.9, respectively. That is, there was a shift in the optimum equivalence ratio for lowest CO emissions, towards stoichiometric, with an increase in EGR. The UHC emissions
were highest for n-heptane, followed by ethanol, DME and the lowest being that of MB over most equivalence ratios. The range of equivalence ratios, for a stable flame, also decreased with increasing EGR. It has been demonstrated that equivalence ratios close to stoichiometric can be used with increasing EGR for a given turbine inlet temperature [34, 39, 42]. In order to achieve high gas turbine thermodynamic cycle efficiency, the design outlet temperature of the combustor is maintained close to the maximum turbine inlet temperature, which is limited by the current state of the art in gas turbine blade materials. Higher overall air-fuel ratios are employed to cool the flow to the design value. Since, the use of EGR, inherently lowers the flame temperatures, higher equivalence ratios can be employed for a given turbine inlet temperature.

In Fig. 4-43, the variation of EI UHC with combustion efficiency has been depicted. The UHC emissions increase significantly for lower combustion efficiencies. The plot is
self-explanatory, since the UHC and CO emissions in the exhaust are a direct measure of combustion inefficiency.

Figure 4-37. Comparison of blowout residence time as a function of blowout equivalence ratio for Ethanol, DME, MB, n-Heptane fuels at EGR = 0.0 and 2.0, $T_A = \text{EGR} = 700$ K, $P = 202.65$ kPa (2 atm).

Figure 4-44 shows the plot of combustion efficiency versus temperature for all fuels. Clearly, all biofuels, namely, MB, DME and ethanol have a superior or comparable emissions performance as compared to n-heptane at EGR of 0.0 and 2.0. At an EGR of 2.0, as is evident from the plot, the overall impact on combustion efficiency due to a change in fuel is substantially dampened out. For example, at an EGR of 0.0, the overall efficiencies vary between 0.80 to 0.98 while for an EGR of 2.0, the combustion efficiency variations are limited to the range of 0.96 to 1.00. This further confirms the improved fuel-flexibility of the PoWER system. At the same time, the limits of operability in temperature are considerably narrower, making the system vulnerable to flame quenching in cold spots.
Figure 4-38. Comparison of blowout equivalence ratio as a function of blowout mass flow rate for Ethanol, DME, MB, n-Heptane fuels at EGR = 0.0 and 2.0, EGR\( T_A = 700 \text{ K}, \ P = 202.65 \text{ kPa (2 atm).} \)

Figure 4-39. Comparison of flame temperature as a function of equivalence ratio for Ethanol, DME, MB, n-Heptane fuels at EGR = 0.0 and 2.0, \( T_A = \text{EGRT} = 700 \text{ K}, \ \tau_{res} = 10.0 \text{ ms, } P = 202.65 \text{ kPa (2 atm).} \)
Figure 4-40. Comparison of combustion efficiency as a function of equivalence ratio for Ethanol, DME, MB, n-Heptane fuels at EGR = 0.0 and 2.0, $T_A = \text{EGRT} = 700 \text{ K}$, $\tau_{res} = 10.0 \text{ ms}$, $P = 202.65 \text{ kPa (2 atm)}$.

Figure 4-41. Comparison of CO emission index as a function of equivalence ratio for Ethanol, DME, MB, n-Heptane fuels at EGR = 0.0 and 2.0, $T_A = \text{EGRT} = 700 \text{ K}$, $\tau_{res} = 10.0 \text{ ms}$, $P = 202.65 \text{ kPa (2 atm)}$. 
Figure 4-42. Comparison of UHC emission index as a function of equivalence ratio for Ethanol, DME, MB, n-Heptane fuels at EGR = 0.0 and 2.0, \( T_A = \text{EGRT} = 700 \text{ K}, \tau_{res} = 10.0 \text{ ms}, P = 202.65 \text{ kPa (2 atm)} \).

Figure 4-43. Comparison of UHC emission index as a function of combustion efficiency for Ethanol, DME, MB, n-Heptane fuels at EGR = 0.0 and 2.0, \( T_A = \text{EGRT} = 700 \text{ K}, \tau_{res} = 10.0 \text{ ms}, P = 202.65 \text{ kPa (2 atm)}, \phi = 0.4-1.0 \).
Figure 4-44. Comparison of combustion efficiency as a function of flame temperature for Ethanol, DME, MB, n-Heptane fuels at EGR = 0.0 and 2.0, $T_A = \text{EGRT} = 700 \text{ K}$, $\tau_{res} = 10.0 \text{ ms}$, $P = 202.65 \text{ kPa (2 atm)}$, $\phi=0.4-1.0$. 
4.3 Case Study 3: Study of EGR Temperature/EGR level on Ethanol Blowout Limits

The trends in ethanol fuel blowout limits were investigated for operating conditions $P= 202650$ Pa (2 atm) and $V = 0.00258$ m$^3$ (15.71 in$^3$) and $\phi = 1.0$, varying EGR values to 0.0, 0.5, 1.0, 1.5, 2.0, and EGRT to 400, 600, 800, 1000, 1200 K. Figures 4-45 through 4-48 show the trends in flame temperature, LP, residence time and total mass flow rate at the blowout limit, respectively, as a function of varying EGR and EGR temperature. The blowout temperature, as shown in figure 4-45 varied linearly with EGR temperature, and non-linearly with EGR level, as is apparent from the spacing between predicted trends. A nearly logarithmic variation can be observed for blowout LP, residence time and total mass flow rate, with varying EGR temperature. The degree of non-linearity (on log scale) was found to increase with increasing EGR. The LP and total mass flow rate decreased, while residence time increased at blowout, with increasing EGR. The trends indicate a sharp drop in blowout stability with increasing EGR, while an increase in stability with temperature. Additionally, the effect of temperature was orders of magnitude stronger at higher EGR.

In figures 4-49 through 4-51 the blowout residence time was plotted against OH, H and CO mass fractions, respectively. The trends showed a strong dependence on the species mass fractions, and the predictions were found to fall nearly on a single curve (with some scatter), irrespective of the EGR flow and temperature. These results were encouraging, and we subsequently plotted normalized predictions for various parameters, in order to collapse the predictions to a single curve. The predictions were normalized to the corresponding values for the zero EGR case (subscripted with 0).

The plot of normalized blowout residence time vs. normalized blowout temperature as shown in figure 4-52 collapsed the model predictions to a nearly single line, suggesting a strong temperature effect on blowout limits. The plot of normalized blowout LP vs. normalized blowout temperature is shown in figure 4-53. Similarly, normalized blowout LP
Figure 4-45. Comparison of blowout flame temperature for ethanol fuel as a function of EGR temperature at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, φ = 1.0, P = 202.65 kPa (2 atm).

vs. normalized OH and CO mass fractions were plotted in figure 4-54 and figure 4-55, and the predictions collapsed to a single line. A remarkable dependence on OH concentrations was found. This is of great importance to experimentalists, since OH emissions have been used to study flame structure in flameless combustion. It is well known that OH emissions correlate well with luminosity of the system and the heat release rate. Moreover, the normalized loading parameter versus OH mass fraction predictions for stable operating points may also explain the sudden drop in luminosity with increasing EGR (for a constant EGR temperature), as the operating point jumps to a lower point on the normalized LP vs. OH mass fraction trend line. Hence, this curve might be of significance to demarcate the transitioning into the flameless regime. The OH emissions are generally measured using more expensive instrumentation such as chemiluminescence or LIF. Hence, we examined the correlation of normalized LP predictions with normalized CO, which may be measured using relatively inexpensive hardware. Another benefit of such a correlation would be that, CO concentration is a strong function of combustion efficiency. Hence,
combustion efficiency could be used to indicate a ‘blowout margin.’ The normalized LP values were found to correlate well with the normalized CO values.

Figure 4-46. Comparison of blowout loading parameter for ethanol fuel as a function of EGR temperature at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, \( \phi = 1.0 \), \( P = 202.65 \) kPa (2 atm).

Figure 4-56 shows the variation of ignition delay with equilibrium flame temperature at various EGR levels. The ignition delay was calculated from constant pressure batch reactor calculations, based on the characteristic time delay for attainment of maximum OH concentration. The result shows that the equilibrium temperature for the zero EGR case would need to be increased to attain a lower ignition delay comparable to that for a non-zero EGR case (by increasing inlet temperature). Alternately, comparing cases at fixed equilibrium temperature, the cases with higher EGR would also require higher inlet temperature, and thus would have a lower ignition delay. On the contrary, the trends plotted in figure 4-57 had a very strong correlation of the ignition delay with respect to the inlet temperature, for all EGR. Surprisingly, the ignition delay was found to drop with EGR, and may be attributed to the presence of reactive intermediates in the EGR stream, as suggested by Kalb and Sattelmayer [16]. Figure 4-58 shows the variation in
ignition delay with EGR at a fixed reactant mixture temperature of 2600 K. In figure 4-59 blowout residence time has been plotted against ignition delay. The ignition delays plotted corresponded to the equilibrium temperature for the steady state compositions of combustor CSTR, at various blowout LP. These equilibrium temperatures were far lower than the equilibrium temperatures calculated in the batch reactor simulations, to estimate ignition delays. As a result, the ignition delays at the CSTR conditions had to be extrapolated, and therefore may be far from accurate. However, the interest behind the ignition delay predictions was to correlate the ignition numbers with LP, and obtain at least qualitative trends from the analysis. The trend of LP as a function of the ratio of residence time to ignition delay (ignition number) has been depicted in figure 4-60. The blowout LP values varied nearly linearly with the ignition number on a log-log plot, at EGR = 0.0. However, strong non-linearities surfaced with increasing EGR for predictions at the lower LP values (for lower EGR temperatures). Finally, normalized LP versus normalized ignition number has been shown in figure 4-61, for various EGR values. This figure shows a significant increase in ignition number and a corresponding decrease in loading parameter, at higher EGR and lower EGRT, when compared with the EGR = 0.0 case. However, it was observed that at reasonably low EGR the normalized ignition number at blowout may decrease with decreasing EGRT before increasing, while normalized blowout loading parameter decreases monotonically. As a result, depending on the EGRT, the normalized ignition number may correspond to different normalized blowout loading parameters (non-unique), especially at low EGR.

The effect of pressure on flame blowout has been depicted in figures 4-62 through 4-65. The blowout limits were reduced as the pressure was reduced, predominantly due to weakening of the heat release rate. Figure 4-62 shows a reduction in flame temperature with decreasing pressure. The effect of pressure seemed to be more pronounced when operating with EGR, as compared to the open cycle (OC) mode, as seen in figures 4-63 through 4-65 for blowout LP, residence time and blowout mass flow rate, respectively.
Ethanol fuel, $\phi=1.0$, $P=202.65$ kPa (2 atm)

Figure 4-47. Comparison of blowout residence time for ethanol fuel as a function of EGR temperature at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, $\phi = 1.0$, $P = 202.65$ kPa (2 atm).

Figure 4-48. Comparison of blowout mass flow rate for ethanol fuel as a function of EGR temperature at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, $\phi = 1.0$, $P = 202.65$ kPa (2 atm).
Figure 4-49. Comparison of blowout residence time for ethanol fuel as a function of OH
species mass fraction at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, EGRT = 400, 600, 800,
1000, 1200 K, $\phi = 1.0$, P = 202.65 kPa (2 atm).

Figure 4-50. Comparison of blowout residence time for ethanol fuel as a function of H
species mass fraction at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, EGRT = 400, 600, 800,
1000, 1200 K, $\phi = 1.0$, P = 202.65 kPa (2 atm).
Figure 4-51. Comparison of blowout residence time for ethanol fuel as a function of CO species mass fraction at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, EGR T = 400, 600, 800, 1000, 1200 K, φ = 1.0, P = 202.65 kPa (2 atm).

Figure 4-52. Comparison of normalized residence time for ethanol fuel as a function of normalized flame temperature at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, EGR T = 400, 600, 800, 1000, 1200 K, φ = 1.0, P = 202.65 kPa (2 atm).
Figure 4-53. Comparison of normalized blowout loading parameter for ethanol fuel as a function of normalized flame temperature at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, EGRT = 400, 600, 800, 1000, 1200 K, \( \phi = 1.0 \), P = 202.65 kPa (2 atm).

Figure 4-54. Comparison of normalized blowout loading parameter for ethanol fuel as a function of normalized OH species mass fraction at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, EGRT = 400, 600, 800, 1000, 1200 K, \( \phi = 1.0 \), P = 202.65 kPa (2 atm).
Figure 4-55. Comparison of normalized blowout loading parameter for ethanol fuel as a function of normalized CO species mass fraction at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, EGRT = 400, 600, 800, 1000, 1200 K, φ = 1.0, P = 202.65 kPa (2 atm).

Figure 4-56. Comparison of ignition delay for ethanol fuel as a function of equilibrium flame temperature at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, reactant mixture inlet temperature 1200 to 2500 K, φ = 1.0, P = 202.65 kPa (2 atm).
Figure 4-57. Comparison of ignition delay for ethanol fuel as a function of reactant mixture inlet temperature at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, $\phi = 1.0$, $P = 202.65$ kPa (2 atm).

Figure 4-58. Variation of ignition delay for ethanol fuel as a function of EGR at reactant mixture inlet temperature = 2600 K, $\phi = 1.0$, $P = 202.65$ kPa (2 atm).
Figure 4-59. Comparison of blowout residence time for ethanol fuel as a function of ignition delay at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, EGR T = 400, 600, 800, 1000, 1200 K, \( \phi = 1.0, \) P = 202.65 kPa (2 atm).

Figure 4-60. Comparison of blowout loading parameter as a function of ignition number at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, EGR T = 400, 600, 800, 1000, 1200 K, \( \phi = 1.0, \) P = 202.65 kPa (2 atm).
Figure 4-61. Comparison of normalized blowout loading parameter as a function of normalized ignition number at EGR = 0.0, 0.5, 1.0, 1.5, 2.0, EGRT = 400, 600, 800, 1000, 1200 K, $\phi = 1.0$, $P = 202.65$ kPa (2 atm).
Figure 4-62. Comparison of blowout flame temperature as a function of air stream/EGR temperature at EGR=0.0 and 2.0, P = 2.0, 1.5, 1.0, 0.5 atm and $\phi = 1.0$.

Figure 4-63. Comparison of blowout loading parameter as a function of air stream/EGR temperature at EGR=0.0 and 2.0, P = 2.0, 1.5, 1.0, 0.5 atm and $\phi = 1.0$. 
Figure 4-64. Comparison of blowout residence time as a function of air stream/EGR temperature at EGR=0.0 and 2.0, P = 2.0, 1.5, 1.0, 0.5 atm and $\phi = 1.0$. 

Figure 4-65. Comparison of blowout mass flow rate as a function of air stream/EGR temperature at EGR=0.0 and 2.0, P = 2.0, 1.5, 1.0, 0.5 atm and $\phi = 1.0$. 

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4.4 Case Study 4: A Study of the Effect of EGR Temperature/EGR level/Residence Time/Equivalence Ratio on Soot Formation (Acetylene Fuel Combustion)

Several cases, as described in section 3.3, were run in order to isolate the effects of system parameters such as EGR, EGR temperature, equivalence ratio and residence time. The results of the simulations have been presented below.

4.4.1 Effect of EGR

The effect of EGR on emissions corresponds to case 1 (EGR = 0.0-5.0, $\phi = 2.0$, $\tau_{res} = 1.0$, EGRT = 1000 K) in section 3.3, and the results have been shown in figures 4-66 through 4-71. The flame temperature drops monotonically with increasing EGR, as shown in figure 4-66. Figure 4-67 shows a plot of UHC emission index as a function of EGR. The UHC emission index was found to increase with EGR, until an EGR of 3.0, after which it was found to be nearly constant. The CO emission index shown in figure 4-68, on the other hand, decreased initially with EGR, and eventually stabilized beyond an EGR of about 2.5. C$_2$H$_2$ has been shown to be an important growth species in the soot formation mechanism, and has been plotted in figure 4-69. The combustion efficiency was found to increase slightly and then decrease with increasing EGR, as shown in figure 4-70. Note that the combustion efficiencies are very low, because the residence time chosen for this study was low (1 ms).

The variation of emission indices of four polyaromatic hydrocarbons (PAH) molecules - benzene ($A_1$), naphthalene ($A_2$), anthracene ($A_3$) and pyrene ($A_4$) has been presented in figure 4-71. The emission indices for all PAH molecules modeled increased to a maximum for EGR of about 2.0 and then decreased. This is not surprising, since vitiation of the reactants with EGR has a strong thermal effect. As a result, the characteristic “soot-bell” like temperature dependence was reflected in the trends of the PAH molecules (soot precursors) with EGR, as is evident in figure 4-71, corresponding to a drop in temperature from approx. 2200 K (at EGR = 0.5) to approx. 1300 K (at EGR = 5). At high temperatures, the oxidative reactions become predominant, reducing the soot
precursor concentrations. On the other hand, at very low temperatures, soot formation rates are low due to insufficient radical concentrations, contributing to the low rates of hydrogen abstraction reactions.

![Flame temperature vs EGR](image)

**Figure 4-66.** Variation of flame temperature for acetylene fuel as a function of EGR at EGRT = 1000 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

![EI UHC vs EGR](image)

**Figure 4-67.** Variation of UHC emission index for acetylene fuel as a function of EGR at EGRT = 1000 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Figure 4-68. Variation of CO emission index for acetylene fuel as a function of EGR at EGRT = 1000 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Figure 4-69. Variation of $C_2H_2$ emission index for acetylene fuel as a function of EGR at EGRT = 1000 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Combustion efficiency

Acetylene fuel, \( P=202.65 \text{ kPa}(2 \text{ atm}) \)
EGRT=1000 K, \( \phi=2.0, \tau_{\text{res}}=1.0 \text{ ms} \)

Figure 4-70. Variation of combustion efficiency for acetylene fuel as a function of EGR at EGRT = 1000 K, \( \phi = 2.0, \tau_{\text{res}} = 1.0 \text{ ms} \), \( P = 202.65 \text{ kPa} \ (2 \text{ atm}) \).

EGR

Combustion efficiency \( \eta_c \)

EI \( A_i \) (PAHs) [g/kg]

EGRT=1000 K, \( \phi = 2.0, \tau_{\text{res}} = 1.0 \text{ ms} \)
Acetylene fuel, \( P=202.65 \text{ kPa}(2 \text{ atm}) \)

Figure 4-71. Comparison of PAH emission indices for acetylene fuel as a function of EGR at EGRT = 1000 K, \( \phi = 2.0, \tau_{\text{res}} = 1.0 \text{ ms} \), \( P = 202.65 \text{ kPa} \ (2 \text{ atm}) \).
4.4.2 Effect of EGR Temperature

The effect of EGR temperature (case 2 in section 3.3 with parameters EGRT = 400-1200 K, EGR = 0.0 and 2.0, φ = 2.0, τ_{res} = 1.0) on soot precursor molecules was modeled. Figures 4-72 through 4-79 depict the effect of EGR temperature for EGR of 0 and 2. The flame temperature was found to vary linearly with increasing EGR temperature as plotted in figure 4-72, with the slope dependent on EGR. The UHC and CO emission index trends with respect to EGR temperature have been presented in figure 4-73 and figure 4-74, respectively. At zero EGR, the emission indices for both CO and UHC were nearly independent of air stream/EGR temperature (the inlet air temperature was varied simultaneously with EGR temperature). On the other hand, at EGR of 2.0, the EI UHC decreased while EI CO increased with EGR temperature. The C₂H₂ concentrations, as shown in figure 4-75, decreased with EGRT (and inlet air temperature), for both EGR of 0.0 and EGR 2.0.

![Figure 4-72. Comparison of flame temperature for acetylene fuel as a function of air stream/EGR temperature at EGR = 0.0 and EGR = 2.0, φ = 2.0, τ_{res} = 1.0 ms, P = 202.65 kPa (2 atm).]
The combustion efficiency was found to have opposite trends at EGR 0.0 and EGR 2.0, with varying EGR temperatures. It can be seen from figure 4-76 that combustion efficiency improved remarkably with EGRT, for EGR = 2.0, while it dropped slightly for EGR = 0.0. It may also be noted that the EI UHC and EI C\textsubscript{2}H\textsubscript{2} values are much higher for EGR of 2.0, suggestive of more favorable sooting conditions. In addition, the EI C\textsubscript{2}H\textsubscript{2} concentrations dropped at a lower rate with increasing EGRT for EGR of 2.0, as compared to EGR of 0.0. The PAH emission indices (EI A\textsubscript{i}, for i=1,2,3 and 4) have been plotted in figure 4-77 to figure 4-79. The PAH emission indices were higher across all EGR temperatures for EGR of 2.0, compared to the EGR = 0.0 case. This is not surprising since, the flame temperatures for EGR = 0.0 case were higher than 2200 K, indicating oxidizing regime, while the EGR = 2.0 case had flame temperatures in the 1400-2100 K range, which is the favorable soot formation regime.

![Figure 4-73. Comparison of UHC emission index for acetylene fuel as a function of air stream/EGR temperature at EGR = 0.0 and EGR = 2.0, φ = 2.0, τ\textsubscript{res} = 1.0 ms, P = 202.65 kPa (2 atm).](image-url)
Figure 4-74. Comparison of CO emission index for acetylene fuel as a function of air stream/EGR temperature at EGR = 0.0 and EGR = 2.0, \( \phi = 2.0 \), \( \tau_{res} = 1.0 \) ms, \( P = 202.65 \) kPa (2 atm).

Figure 4-75. Comparison of \( \text{C}_2\text{H}_2 \) emission index for acetylene fuel as a function of air stream/EGR temperature at EGR = 0.0 and EGR = 2.0, \( \phi = 2.0 \), \( \tau_{res} = 1.0 \) ms, \( P = 202.65 \) kPa (2 atm).
Acetylene fuel, $P=202.65$ kPa (2 atm)  
$\phi=2.0$, $\tau_{res}=1.0$ ms  

Figure 4-76. Comparison of combustion efficiency for acetylene fuel as a function of air stream/EGR temperature at EGR = 0.0 and EGR = 2.0, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Figure 4-77. Comparison of PAH emission indices for acetylene fuel as a function of air stream/EGR temperature at EGR = 0.0, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Figure 4-78. Comparison of PAH emission indices for acetylene fuel as a function of EGR temperature at EGR=0.0, $\phi=2.0$, $\tau_{res}=5.0$ ms.

Figure 4-79. Comparison of PAH emission indices for acetylene fuel as a function of EGR temperature at EGR=0.0, $\phi=2.0$, $\tau_{res}=5.0$ ms.
4.4.3 Effect of Equivalence Ratio

The variation of combustion characteristics and soot precursors with equivalence ratio (case 3 in section 3.3 with parameters \( \phi = 0.5\text{-}5.0 \), \( \text{EGR} = 0.0 \) and 2.0, \( \tau_{res} = 1.0 \), \( \text{EGRT} = 1000 \text{ K} \)) has been modeled and the results presented in figures 4-80 through 4-85. The flame temperature for \( \text{EGR} = 0.0 \) and \( \text{EGR} = 2.0 \) have been plotted with varying equivalence ratios in figure 4-80. Surprisingly, the equivalence ratio for maximum flame temperature was on fuel-rich side (\( \phi = 1.5 \)) for \( \text{EGR} = 0.0 \), although points between \( \phi = 1.0 \) and \( \phi = 1.5 \) were not modeled. The UHC emissions, plotted in figure 4-81, increased non-linearly with equivalence ratio for \( \text{EGR} = 2.0 \), while it had a minimum at about equivalence ratio of 2.0 for \( \text{EGR} = 0.0 \). The CO emissions shown in figure 4-82, reached a maximum between equivalence ratio of 1.5 and 2.5 and then decreased linearly with increasing equivalence ratio on the fuel-rich side. The EI \( \text{C}_2\text{H}_2 \) values were plotted in figure 4-83. It can be observed that there is a sharp rise in EI \( \text{C}_2\text{H}_2 \) at equivalence ratios between 1.0 and 2.0. Consequently, depending on a threshold minimum \( \text{C}_2\text{H}_2 \) concentration necessary for soot formation, a critical equivalence ratio may be identified below which no soot formation would occur. Moreover, the critical equivalence ratio for \( \text{EGR} = 2.0 \) is likely to be lower than that for \( \text{EGR} = 0.0 \), since the EI \( \text{C}_2\text{H}_2 \) increases rapidly at lower equivalence ratios for \( \text{EGR} = 2.0 \) case. This may be explained by the fact that recirculation of fuel-rich exhaust gases has a tendency of increasing the effective equivalence ratio, increasing the overall sooting. The combustion efficiency was found to decrease non-linearly with equivalence ratio, as shown in figure 4-84. The trends also indicate the crossover of combustion efficiency for \( \text{EGR} = 0.0 \) and 2.0 at an equivalence ratio of about 2.0. The \( \text{EGR} = 2.0 \) had much higher combustion efficiency at equivalence ratios less than 2.0, while beyond the lower combustion efficiency for higher equivalence ratios resulted from higher UHC emissions, compared to \( \text{EGR} = 0.0 \) case. Figures 4-85 and 4-86 indicate the PAH emission indices for \( \text{EGR} = 0.0 \) and 2.0 cases (shown on two
different y-scales for clarity). The EI PAH trends seem to closely follow the EI C$_2$H$_2$ trends, since C$_2$H$_2$ is a key intermediate in the soot formation chain.

![Graph](image)

**Figure 4-80.** Comparison of flame temperature for acetylene fuel as a function of equivalence ratio at EGR = 0.0 and EGR = 2.0, EGRT = 1000 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Figure 4-81. Comparison of UHC emission index for acetylene fuel as a function of equivalence ratio at EGR = 0.0 and EGR = 2.0, EGRT = 1000 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, P = 202.65 kPa (2 atm).

Figure 4-82. Comparison of CO emission index for acetylene fuel as a function of equivalence ratio at EGR = 0.0 and EGR = 2.0, EGRT = 1000 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, P = 202.65 kPa (2 atm).
Figure 4-83. Comparison of $C_2H_2$ emission index for acetylene fuel as a function of equivalence ratio at EGR = 0.0 and EGR = 2.0, EGRT = 1000 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Figure 4-84. Comparison of combustion efficiency for acetylene fuel as a function of equivalence ratio at EGR = 0.0 and EGR = 2.0, EGRT = 1000 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Figure 4-85. Comparison of PAH emission indices for acetylene fuel as a function of equivalence ratio at EGR = 0.0 and EGR = 2.0, EGRT = 1000 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Figure 4-86. Comparison of PAH emission indices for acetylene fuel as a function of equivalence ratio at EGR = 0.0 and EGR = 2.0, EGRT = 1000 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
4.4.4 Effect of Residence Time

The residence time dependence (case 4 in section 3.3 with parameters \( \tau = 0.1-10.0, \phi = 2.0, \text{EGR} = 0.0 \) and 2.0, \( \text{EGRT} = 1000 \text{ K} \)) for various combustion parameters has been plotted in figures 4-87 through 4-94. For the case of \( \text{EGR} = 0.0 \), the flame temperature, EI UHC, EI \( \text{C}_2\text{H}_2 \), EI CO and combustion efficiency values nearly stabilize in less than 2 ms, while those for the case of \( \text{EGR} = 2.0 \) do not stabilize until 10 ms. From the plots of emission indices of PAH precursors, it can be seen that the \( \text{EGR} = 0.0 \) case (figure 4-92) was in oxidizing regime (PAH concentrations decrease with time) while \( \text{EGR} = 2.0 \) case (figure 4-93) was in the soot formation regime (PAH concentrations increase with time). The decrease in PAH concentrations in \( \text{EGR} = 0.0 \) case, appears to be resulting from decrease in \( \text{C}_2\text{H}_2 \) concentrations. On the other hand, it seems likely that the decrease in \( \text{C}_2\text{H}_2 \) concentration in \( \text{EGR} = 2.0 \) case may be resulting from polymerization reactions that eventually result in formation of aromatic structures.

![Figure 4-87](image.png)

Figure 4-87. Comparison of flame temperature for acetylene fuel as a function of residence time at \( \text{EGR} = 0.0 \) and \( \text{EGR} = 2.0, \phi = 2.0, \text{EGRT} = 1000 \text{ K}, P = 202.65 \text{ kPa (2 atm)}. \)
Figure 4-88. Comparison of UHC emission index for acetylene fuel as a function of residence time at EGR = 0.0 and EGR = 2.0, φ = 2.0, EGR T = 1000 K, P = 202.65 kPa (2 atm).

Figure 4-89. Comparison of CO emission index for acetylene fuel as a function of residence time at EGR = 0.0 and EGR = 2.0, φ = 2.0, EGR T = 1000 K, P = 202.65 kPa (2 atm).
Figure 4-90. Comparison of $C_2H_2$ emission index for acetylene fuel as a function of residence time at EGR = 0.0 and EGR = 2.0, $\phi = 2.0$, EGRT = 1000 K, $P = 202.65$ kPa (2 atm).

Figure 4-91. Comparison of combustion efficiency for acetylene fuel as a function of residence time at EGR = 0.0 and EGR = 2.0, $\phi = 2.0$, EGRT = 1000 K, $P = 202.65$ kPa (2 atm).
Figure 4-92. Comparison of PAH emission indices for acetylene fuel as a function of residence time at EGR = 0.0, φ = 2.0, EGRT = 1000 K, P = 202.65 kPa (2 atm).

Figure 4-93. Comparison of PAH emission indices for acetylene fuel as a function of residence time at EGR = 2.0, φ = 2.0, EGRT = 1000 K, P = 202.65 kPa (2 atm).
Figure 4-94. Comparison of PAH emission indices for acetylene fuel as a function of residence time at EGR = 0.0 and EGR = 2.0, $\phi = 2.0$, EGRT = 1000 K, P = 202.65 kPa (2 atm).
4.5 Case Study 5: Soot Particle Growth and Oxidation in Vitiated Combustion

The formation of particulate soot in presence of EGR was investigated and the results have been presented in this section. Figure 4-95 depicts the effect of EGR on soot formation. It was found that the soot volume fraction increased with EGR, for the flame temperatures between 1500 to 2000 K. From the plot of soot particle diameter versus the flame temperature shown in figure 4-96, it may be inferred that the particle diameter increased with EGR, and that there was an increasing dominance of the soot growth and/or coagulative processes at higher temperatures (between 1500-2000 K). Figure 4-97 shows the plot of soot surface area with respect to flame temperature. An increase of the soot surface area at lower temperature may be attributed to the nucleation of soot particles, and an increase in the soot particle sizes due to the growth processes. It is well-known that over about 95% of the observed soot volume increase may be attributed to the soot surface chemistry [161]. The decrease in the soot surface area at higher temperatures may be attributed to the coagulation of soot particles.

The variation of the absolute values of zero\textsuperscript{th} moment generation rates for the particle distribution with flame temperature are plotted in figure 4-98 and figure 4-99, for EGR 0.0 and 2.0 respectively. It represents the rate of change of the number density of the soot particles. It may be observed that the contribution of both the nucleation (positive effect) and coagulation processes (negative effect) to the change in number densities is high, while surface growth has no effect on particle number densities. The particles nucleate at a much larger rate, however, they coagulate to grow in size, with a consequent decrease in number densities. As a result, the net effect is a much lower rate of increase in number densities. A comparison of the absolute values of the zero\textsuperscript{th} moment generation rates for EGR of 0.0 and 2.0 has been presented in figure 4-99. Surprisingly, a suppression of nucleation and coagulation rates with EGR was observed, despite the increase in soot volume fraction. This may be rationalized by the fact that most of the increase in
Figure 4-95. Comparison of soot volume fraction for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Figure 4-96. Comparison of average soot particle diameter for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
soot volume fraction comes from the surface chemistry. On the other hand, the surface chemistry, has no effect on particle population, while it does affect the size.

![Graph showing comparison of average soot particle surface area for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0, φ = 2.0, τ_res = 1.0 ms, P = 202.65 kPa (2 atm).](image)

Figure 4-97. Comparison of average soot particle surface area for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0, φ = 2.0, τ_res = 1.0 ms, P = 202.65 kPa (2 atm).

The rate of change of total mass of soot particles has been characterized by the absolute values of the first moment generation rates, plotted with respect to flame temperatures in figure 4-101 and figure 4-102 for EGR = 0.0 and EGR = 2.0, respectively. It may be observed that majority of the surface growth may be attributed to surface chemistry, and coagulation processes play no role. On comparing these rates for EGR = 0.0 and EGR = 2.0, shown in figure 4-103, we found that surface chemistry was reduced with EGR. The natural question to ask at this point then would be that, what would cause an increase in soot volume fraction, if the rates of nucleation, coagulation, as well as surface chemistry reduced with EGR? On a closer inspection, it may be observed that the soot formation process was being controlled by the residence time of the fresh reactant stream. In order to hold the total residence time fixed, all the mass flows were scaled with increasing
EGR. This necessitated reduction in fresh fuel and air stream mass flows, increasing the residence time of fresh reactants from this stream. Given the assumption of homogeneity of the model, it may be reasoned that the EGR composition was nearly the same as the product composition. As a result, one dominant effect of increasing EGR, for a given constant flame temperature would be increasing the residence time of the fresh reactants. From results presented in Brown et al. [159], it can be seen that the soot volume fraction increases with residence time, provided that the temperatures were within the critical limits of the soot formation regime. Therefore, despite a suppression in the rates of the soot growth processes, the increased residence time of the fresh reactant stream due to increased EGR, ultimately results in higher soot volume fractions.

![Graph showing soot production rate vs. flame temperature](image)

Figure 4-98. Comparison of zero\textsuperscript{th} soot moment production rate contributions (nucleation, coagulation, surface growth) for acetylene fuel as a function of flame temperature at $\phi = 2.0$, EGR = 0.0, $\tau_{\text{res}} = 1.0$ ms, P = 202.65 kPa (2 atm).
Figure 4-99. Comparison of zero\textsuperscript{th} soot moment production rate contributions (nucleation, coagulation, surface growth) for acetylene fuel as a function of flame temperature at $\phi = 2.0$, EGR = 2.0, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Figure 4-100. Comparison of zero\textsuperscript{th} soot moment production rate contributions (nucleation, coagulation, surface growth) for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Figure 4-101. Comparison of first soot moment production rate contributions (nucleation, coagulation, surface growth) for acetylene fuel as a function of flame temperature at $\phi = 2.0$, EGR = 0.0, $\tau_{res} = 1.0$ ms, P = 202.65 kPa (2 atm).

Figure 4-102. Comparison of first soot moment production rate contributions (nucleation, coagulation, surface growth) for acetylene fuel as a function of flame temperature at $\phi = 2.0$, EGR = 2.0, $\tau_{res} = 1.0$ ms, P = 202.65 kPa (2 atm).
The PAH concentrations were plotted as functions of flame temperature and EGR, as shown in figure 4-104 through figure 4-106. While the PAH concentrations decreased towards higher temperatures, no general trends could be inferred about the effect of EGR, for comparisons at constant flame temperatures.

The absolute values of the effective contributions of C$_2$H$_2$, PAH, OH and O$_2$ to surface growth rate (negative for OH and O$_2$) were plotted with respect to the flame temperature and EGR in figure 4-107 through figure 4-108. It was found that maximum contribution to the soot growth was due to C$_2$H$_2$ addition reactions. The reactions due to OH oxidation were found to be more important at higher temperatures, while the PAH condensation reactions were found to be active at lower temperatures. The effect of EGR, on soot surface chemistry could be summarized as that of lowering of growth
Figure 4-104. Comparison of $A_i$ (PAHs) emission indices for acetylene fuel as a function of flame temperature at $\phi = 2.0$, EGR = 0.0, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Figure 4-105. Comparison of $A_i$ (PAHs) emission indices for acetylene fuel as a function of flame temperature at $\phi = 2.0$, EGR = 2.0, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
rates due to acetylene in the temperatures between 1500-1900 K, a shift in the peak of acetylene contributions, towards the right, and slightly higher oxidation rates on the high temperature end. Therefore, the lower soot growth rates in the lower temperature side, were mainly due to suppression acetylene reactions, while the increased rates on the high temperature side were due a competition between increased oxidation and $C_2H_2$ addition reactions.

The plot in figure 4-110 shows that the trends in soot particle mass density with flame temperature and EGR. The correlations for SN were based on the recommendations of Colket III et al. [141]. However, unrealistic estimates of SN (greater than 100) were obtained, for the calculated soot particle mass densities and hence, are not shown in the plots.

Figure 4-106. Comparison of $A_i$ (PAHs) emission indices for acetylene fuel as a function of flame temperature at $\phi = 2.0$, EGR = 0.0 and EGR = 2.0, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Acetylene fuel, $P=202.65$ kPa (2 atm)
EGR = 0.0, $\phi=2.0$, $\tau_{res}=1.0$ ms

Figure 4-107. Comparison of surface growth rate for acetylene fuel as a function of flame temperature at $\phi = 2.0$, EGR = 0.0, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Acetylene fuel, $P=202.65$ kPa (2 atm)
EGR = 2.0, $\phi=2.0$, $\tau_{res}=1.0$ ms

Figure 4-108. Comparison of surface growth rate contributions (PAH condensation, $C_2H_2$ addition, $O_2$ oxidation, OH oxidation) for acetylene fuel as a function of flame temperature at $\phi = 2.0$, EGR = 2.0, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Figure 4-109. Comparison of surface growth rate contributions (PAH condensation, C$_2$H$_2$ addition, O$_2$ oxidation, OH oxidation) and OH oxidation reactions for acetylene fuel as a function of flame temperature at $\phi = 2.0$, EGR = 0.0 and EGR = 2.0, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Figure 4-110. Comparison of soot mass density for acetylene fuel as a function of flame temperature at $\phi = 2.0$, EGR = 2.0, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
4.6 Comparison of Frenklach and Richter Models of Soot Formation

A comparison of the results based on the models from Frenklach and coworkers and that from the Richter et al. have been presented in figures 4-111 through 4-124. It may be seen that there was generally a very good agreement in EI UHC, EI CO, combustion efficiencies obtained from the models, plotted in figure 4-111, figure 4-112 and figure 4-114, respectively. The results from the frenklach model, seemed to overpredict the values for EI \( \text{C}_2\text{H}_2 \), as seen in figure 4-113. The comparison of the PAH species, namely benzene (A_1), naphthalene (A_2), anthracene (A_3) and pyrene (A_4), predicted from both models has been presented in figures 4-115 through 4-118. These seem to agree pretty well.

The particle bin distributions for EGR = 0.0 and EGR = 2.0 were plotted for temperatures 1500-2000 K, and are shown in figures 4-119 through 4-124. The growth of particle diameters predicted by the Frenklach model in figure 4-96, may be observed as the increase in the concentration of higher mass species, predicted by the Richter model in figures 4-119 through 4-124. We found good agreement from the general trends from both the models.

![Graph](image)

Figure 4-111. Comparison of UHC emission index for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0 (Richter mechanism and Frenklach mechanism), \( \phi = 2.0, \tau_{res} = 1.0 \text{ ms} \).
Figure 4-112. Comparison of CO emission index for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0 (Richter mechanism and Frenklach mechanism), $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Figure 4-113. Comparison of $C_2H_2$ emission index for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0 (Richter mechanism and Frenklach mechanism), $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Figure 4-114. Comparison of combustion efficiency for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0 (Richter mechanism and Frenklach mechanism), $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Figure 4-115. Comparison of $A_1$ emission index for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0 (Richter mechanism and Frenklach mechanism), $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Figure 4-116. Comparison of $A_2$ emission index for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0 (Richter mechanism and Frenklach mechanism), $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Figure 4-117. Comparison of $A_3$ emission index for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0 (Richter mechanism and Frenklach mechanism), $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Figure 4-118. Comparison of $A_4$ emission index for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0 (Richter mechanism and Frenklach mechanism), $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Acetylene fuel, $P=202.65$ kPa (2 atm), $EGR=1500$ K, $\phi=2.0$, $\tau_{res}=1.0$ ms

Figure 4-119. Comparison of bin mass fractions for acetylene fuel as a function of flame temperature at $EGR=0.0$ and $EGR=2.0$, $EGR=T=1500$ K, $\phi=2.0$, $\tau_{res}=1.0$ ms, $P=202.65$ kPa (2 atm).

Acetylene fuel, $P=202.65$ kPa (2 atm), $EGR=1600$ K, $\phi=2.0$, $\tau_{res}=1.0$ ms

Figure 4-120. Comparison of bin mass fractions for acetylene fuel as a function of flame temperature at $EGR=0.0$ and $EGR=2.0$, $EGR=T=1600$ K, $\phi=2.0$, $\tau_{res}=1.0$ ms, $P=202.65$ kPa (2 atm).
Figure 4-121. Comparison of bin mass fractions for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0, EGRT = 1700 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Figure 4-122. Comparison of bin mass fractions for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0, EGRT = 1800 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
Figure 4-123. Comparison of bin mass fractions for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0, EGRT = 1900 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).

Figure 4-124. Comparison of bin mass fractions for acetylene fuel as a function of flame temperature at EGR = 0.0 and EGR = 2.0, EGRT = 2000 K, $\phi = 2.0$, $\tau_{res} = 1.0$ ms, $P = 202.65$ kPa (2 atm).
4.7 Case Study 6: Modeling of Semi-Closed Cycle Engine Characteristics using a Kinetically Equivalent Unvitiated Open-Cycle CSTR System

The analysis for determining a kinetically equivalent OC system for a given SCC system, has been discussed in this section. The main assumptions for the analysis are:

1. Ideal gas mixture is assumed
2. Volume and pressure are constant
3. Spatially homogeneous system
4. The reacting mixture is in steady state

4.7.1 Semiclosed Case

For a CSTR in steady state as shown in figure 3-7A, the species conservation across control volume CV1 may be written given by equation 4–1.

\[
\left( \frac{dm_j}{dt} \right)_{CV} = (\dot{m}_F Y_{F,j} + \dot{m}_A Y_{A2,j} + \dot{m}_R Y_{R,j} - \dot{m}_{ex1} Y_{ex1,j}) + (\bar{M_j} \dot{V} \omega_j) = 0 \quad (4-1)
\]

\[
\left( \frac{dm}{dt} \right)_{CV} = (\dot{m}_F + \dot{m}_A + \dot{m}_R) - \dot{m}_{ex1} = 0 \quad (4-2)
\]

\[
\left[ \rho V_R \frac{h_S(T_{ex})}{dt} \right]_{CV} = (\dot{m}_F h_{F,S} + \dot{m}_A h_{A2,S} + \dot{m}_R h_{R,S}) - V_R \dot{Q}_{gen} - (\dot{m}_{ex1} h_{ex1,S}) = 0 \quad (4-3)
\]

where \( V_R \dot{Q}_{gen} = \left( \sum^{n_S}_{j=0} V_R h_{F,j}(T_0) \omega_j(T_{ex}) \right) \)

The total enthalpy \( h \) may be calculated as a sum of sensible enthalpy \( h_S \) and enthalpy of formation \( h_F(T_0) \), given by equation 4–4.

\[
h = h(T) = h_S(T) + h_F(T_0) = \sum^{n_S}_{j=0} Y_j \left( h_{f,j}(T_0) + \int^{T}_{T_0} c_{p,j}(T) \, dT \right) \quad (4-4)
\]

4.7.2 Open Cycle Case

The conservation equations for an OC system are given by equations equation 4–5 through equation 4–7.
\[
\frac{dm_j}{dt}_{CV} = (\dot{m}_F Y_{F,j} + \dot{m}_A Y_{A1,j} - \dot{m}_{ex2,j}) + (\dot{M}_j V_R \dot{\omega}_j) = 0 \quad (4-5)
\]
\[
\frac{dm}{dt}_{CV} = (\dot{m}_F + \dot{m}_A) - \dot{m}_{ex2} = 0 \quad (4-6)
\]
\[
\left[ \rho V_R \frac{h_S (T_{ex})}{dt} \right]_{CV} = (\dot{m}_F h_{F,S} + \dot{m}_A h_{A,S}) - V_R \dot{Q}_{gen} - Q_L - (\dot{m}_{ex2} h_{ex2,S}) = 0 \quad (4-7)
\]

### 4.7.3 Matching Conditions

The matching conditions for a kinetically equivalent OC are based on a match in the exit enthalpies and species production rates. Four equivalent systems were analyzed, as discussed in section 3.3.6.

#### 4.7.3.1 Case A: An adiabatic OC system equivalent to an SCC system, with lower reactant inlet temperatures and larger residence time with matched fresh reactant flows

An adiabatic OC system equivalent to an SCC system as shown in figure 3-7B, with lower inlet temperatures and larger residence time with match fresh reactant flows may be used to simulate the steady state temperatures of an SCC system. The following assumptions were made:

- \([P]_{SCC} = [P]_{OC} \); \([V_R]_{SCC} = [V_R]_{OC}\)
- \([\dot{m}_F]_{SCC} = [\dot{m}_F]_{OC}; [\dot{m}_A]_{SCC} = [\dot{m}_A]_{OC}\)
- \([\dot{\omega}_j]_{SCC} = [\dot{\omega}_j]_{OC}; [\dot{Q}_{gen}]_{SCC} = [\dot{Q}_{gen}]_{OC}\)
- \([h_{ex1}]_{SCC} = [h_{ex1}]_{OC}; [h_{F,S}]_{SCC} = [h_{F,S}]_{OC}\)
- \([Y_{j,F}]_{SCC} = [Y_{j,F}]_{OC}; [Y_{j,A}]_{SCC} = [Y_{j,A}]_{OC}; [Y_{j,ex1}]_{SCC} = [Y_{j,ex1}]_{OC}; [Y_{j,R}]_{SCC} = [Y_{j,R}]_{SCC}\)

The scaling factor for the total mass flows, defined by \(\gamma_A\), is given by equation 4-8.

Matching of the exit enthalpies, obtained from the energy conservation gives equation 4-9.

\[
\gamma_A = \frac{[\dot{m}_{ex2}]_{OC}}{[\dot{m}_{ex1}]_{SCC}} = \frac{[\dot{m}_F + \dot{m}_A]_{OC}}{[\dot{m}_F + \dot{m}_A + \dot{m}_R]_{SCC}} \quad (4-8)
\]
\[
\dot{m}_A \left[(h_{A,S})_{SCC} - (h_{A,S})_{OC}\right] = \dot{m}_R \left[(h_{ex1,S})_{SCC} - (h_{R,S})_{SCC}\right] \quad (4-9)
\]

This allows calculation of the inlet air enthalpy using equation 4–10. The species balance is automatically satisfied for the given simplifying assumptions.

\[
(T_A)_{OC} = (T_A)_{SCC} - \frac{EGR}{C_{P,A}} \left[(h_{ex1,S})_{SCC} - (h_{R,S})_{SCC}\right] \quad (4-10)
\]

### 4.7.3.2 Case B: An adiabatic OC system equivalent to an SCC system, with lower reactant inlet temperatures and matched residence time

An adiabatic OC system equivalent to an SCC system as shown in figure 3-7B, with lower reactant inlet temperatures and matched residence time may be used to simulate the steady state temperatures of an SCC system. The following assumptions were made:

- \([P]_{SCC} = [P]_{OC}; [V_R]_{SCC} = [V_R]_{OC}\)
- \([\dot{m}_{ex1}]_{SCC} = [\dot{m}_{ex2}]_{OC}\)
- \([\dot{\omega}_j]_{SCC} = [\dot{\omega}_j]_{OC}; [\dot{Q}_{gen}]_{SCC} = [\dot{Q}_{gen}]_{OC}\)
- \([h_{ex1}]_{SCC} = [h_{ex2}]_{OC}; [h_{F,S}]_{SCC} = [h_{F,S}]_{OC}\)
- \([Y_{j,F}]_{SCC} = [Y_{j,F}]_{OC}; [Y_{j,A}]_{SCC} = [Y_{j,A}]_{OC}; [Y_{j,ex1}]_{SCC} = [Y_{j,ex1}]_{OC}; [Y_{j,R}]_{SCC} = [Y_{j,R}]_{OC}\)

The scaling factor for the total mass flows, defined by \(\gamma_A\), is given by equation 4–11. Hence the scaling of fresh air mass flows may be calculated from equation 4–12.

\[
\gamma_A = \frac{[\dot{m}_{ex2}]_{OC}}{[\dot{m}_{ex1}]_{SCC}} = 1 \quad (4-11)
\]

\[
\gamma_B = \frac{[\dot{m}_A]_{OC}}{[\dot{m}_A]_{SCC}} = \frac{\left[\frac{\phi}{\sigma_{st.}} + 1 + EGR\right]_{SCC}}{\left[\frac{\phi}{\sigma_{st.}} + 1\right]_{OC}} \quad (4-12)
\]

Using the definitions of \(\gamma_A\) and \(\gamma_B\), and matching the species balances for OC and SCC systems, gives equation 4–13 which further simplifies to equation 4–14.
\[
\dot{m}_R Y_{R,j} + [(\dot{m}_F)_{SCC} - (\dot{m}_F)_{OC}] Y_{F,j} + [(\dot{m}_A)_{SCC} - (\dot{m}_A)_{OC}] Y_{A,j} = 0 \quad (4–13)
\]

\[
EGR (Y_{R,j}) + \left[ Y_{F,j} \alpha_{st} + Y_{A,j} \right] (1 - \gamma_B) = 0 \quad (4–14)
\]

This implies that the decrease in the species mass fractions from fresh air and fuel mass flows in the SCC system, is equal to the mass fractions added from the fresh stream. This equation is automatically satisfied from the total mass balance, for the given assumptions. Matching of the exit enthalpies, obtained from the energy conservation gives equation 4–15.

\[
[(\dot{m}_F h_{F,S})_{SCC} - (\dot{m}_F h_{F,S})_{OC}] + [(\dot{m}_A h_{A,S})_{SCC} - (\dot{m}_A h_{A,S})_{OC}] + \dot{m}_R (h_{R,S})_{SCC} = 0 \quad (4–15)
\]

This means that the energy supplied by the EGR stream must be balanced off by the inlet enthalpies of the fuel and air streams in the OC. Further simplification allows calculation of the inlet air enthalpy using equation 4–16. The species balance is automatically satisfied for the given simplifying assumptions.

\[
(T_A)_{OC} = \frac{[(h_{A,S})_{SCC} + \frac{\phi}{\alpha_{st}} (1 - \gamma_B)(h_{F,S})_{SCC}] + EGR (h_{R,S})_{SCC}}{\gamma_B C_{P,A}} \quad (4–16)
\]

**4.7.3.3 Case C: A non-adiabatic OC system equivalent to an SCC system, with a positive heat loss and larger residence time with matched fresh reactant flows.**

An adiabatic OC system equivalent to an SCC system as shown in figure 3-7C, with a positive heat loss and larger residence time with matched fresh reactant flows may be used to simulate the steady state temperatures of an SCC system. The following assumptions were made:

- \([P]_{SCC} = [P]_{OC}; [V_R]_{SCC} = [V_R]_{OC}\)
\[ \dot{m}_F \text{SCC} = [\dot{m}_F]_{OC}; \] 
\[ \dot{m}_A \text{SCC} = [\dot{m}_A]_{OC} \]

\[ [\dot{\omega}_j] \text{SCC} = [\dot{\omega}_j]_{OC}; \] 
\[ [\dot{Q}_{\text{gen}}] \text{SCC} = [\dot{Q}_{\text{gen}}]_{OC} \]

\[ [h_{\text{ex}1}] \text{SCC} = [h_{\text{ex}2}]_{OC}; \] 
\[ [h_{F,S}] \text{SCC} = [h_{F,S}]_{OC} \]

\[ [Y_{j,F}] \text{SCC} = [Y_{j,F}]_{OC}; \] 
\[ [Y_{j,A}] \text{SCC} = [Y_{j,A}]_{OC}; \] 
\[ [Y_{j,\text{ex}1}] \text{SCC} = [Y_{j,\text{ex}2}]_{OC}; \] 
\[ [Y_{j,R}] \text{SCC} = \] 

\[ \gamma_A = \frac{[\dot{m}_{\text{ex}2}]_{OC}}{[\dot{m}_{\text{ex}1}]_{SCC}} = \frac{[\dot{m}_F + \dot{m}_A]_{OC}}{[\dot{m}_F + \dot{m}_A + \dot{m}_R]_{SCC}} \] (4–17)

\[ -Q_L + \dot{m}_R h_{R,S} = [(\dot{m}_{\text{ex}1})_{SCC} - (\dot{m}_{\text{ex}2})_{OC}] h_{\text{ex}1,S} = [\dot{m}_{\text{ex}1}]_{SCC} (1 - \gamma_A) h_{\text{ex}1,S} = \dot{m}_R h_{\text{ex}1,S} \] (4–18)

\[ -Q_L = \dot{m}_R [h_{\text{ex}1,S} - h_{R,S}] \] (4–19)

This shows that the heat loss through the reactor walls of the OC system must equal the heat loss in the EGR stream, as shown in figure 3-7A. The species balance is automatically satisfied for the given simplifying assumptions.

**4.7.3.4 Case D: A non-adiabatic OC system equivalent to an SCC system, with a positive heat loss and matched residence time**

An adiabatic OC system equivalent to an SCC system as shown in figure 3-7C, with a positive heat loss and matched residence time may be used to simulate the steady state temperatures of an SCC system. The following assumptions were made:

\[ [P]_{SCC} = [P]_{OC}; [V_R]_{SCC} = [V_R]_{OC} \]
• $[\dot{m}_{\text{ex}1}]_{\text{SCC}} = [\dot{m}_{\text{ex}2}]_{\text{OC}}$
• $[\dot{\omega}_j]_{\text{SCC}} = [\dot{\omega}_j]_{\text{OC}}$; $[\dot{Q}_{\text{gen}}]_{\text{SCC}} = [\dot{Q}_{\text{gen}}]_{\text{OC}}$
• $[h_{\text{ex}1}]_{\text{SCC}} = [h_{\text{ex}2}]_{\text{OC}}$; $[h_{F,S}]_{\text{SCC}} = [h_{F,S}]_{\text{OC}}$
• $[Y_{j,F}]_{\text{SCC}} = [Y_{j,F}]_{\text{OC}}$; $[Y_{j,A}]_{\text{SCC}} = [Y_{j,A}]_{\text{OC}}$; $[Y_{j,\text{ex}1}]_{\text{SCC}} = [Y_{j,\text{ex}2}]_{\text{OC}}$; $[Y_{j,R}]_{\text{SCC}} = [Y_{j,\text{ex}1}]_{\text{SCC}}$
• $[h_{F,S}]_{\text{SCC}} = [h_{F,S}]_{\text{OC}}$; $[h_{A,S}]_{\text{SCC}} = [h_{A,S}]_{\text{OC}}$
• the system is non-adiabatic

The scaling factor for the total mass flows, defined by $\gamma_A$, is given by equation 4–20. Hence the scaling of fresh air mass flows may be calculated from equation 4–21.

$$\gamma_A = \frac{[\dot{m}_{\text{ex}2}]_{\text{OC}}}{[\dot{m}_{\text{ex}1}]_{\text{SCC}}} = 1 \tag{4–20}$$

$$\gamma_B = \frac{[\dot{m}_A]_{\text{OC}}}{[\dot{m}_A]_{\text{SCC}}} = \frac{\left[\frac{\phi}{\alpha_{st}} + 1 + \text{EGR}\right]_{\text{SCC}}}{\left[\frac{\phi}{\alpha_{st}} + 1\right]_{\text{OC}}} \tag{4–21}$$

Using the definitions of $\gamma_A$ and $\gamma_B$, and matching the species balances for OC and SCC systems, give equation 4–22, which simplifies to equation 4–23.

$$\dot{m}_R Y_{R,j} + [(\dot{m}_F)_{\text{SCC}} - (\dot{m}_F)_{\text{OC}}] Y_{F,j} + [(\dot{m}_A)_{\text{SCC}} - (\dot{m}_A)_{\text{OC}}] Y_{A,j} = 0 \tag{4–22}$$

$$\text{EGR} \left( Y_{R,j} \right) + \left[ Y_{F,j} \frac{\phi}{\alpha_{st}} + Y_{A,j} \right] (1 - \gamma_B) = 0 \tag{4–23}$$

This implies that the decrease in the species mass fractions from fresh air and fuel mass flows in the SCC system, is equal to the mass fractions added from the EGR stream. This equation is automatically satisfied from the total mass balance, for the given assumptions. Matching of the exit enthalpies, obtained from the energy conservation gives equation 4–24.
\[
\left(\dot{m}_F h_{F,S}\right)_{SCC} - (\dot{m}_F h_{F,S})_{OC} + \left(\dot{m}_A h_{A,S}\right)_{SCC} - (\dot{m}_A h_{A,S})_{OC} + \dot{m}_R (h_{R,S})_{SCC} + Q_L = 0
\]

(4–24)

This means that the heat loss must equal the sum of energy supplied by the EGR stream and the differential inlet enthalpies between the SCC and OC systems for the fuel and air streams. Further simplification allows calculation of the inlet air enthalpy using equation 4–25.

\[
Q_L = (\dot{m}_A)_{SCC} \left[ (\gamma_B - 1) \left( h_{A,S} \right)_{SCC} + \frac{\phi}{\alpha_{st.}} (h_{F,S})_{SCC} \right] - EGR (h_{R,S})_{SCC}
\]

(4–25)

The species balance is automatically satisfied for the given simplifying assumptions. The variation of flame temperature, EI UHC, EI CO and EI OH with respect to the air/EGR stream temperature as shown in figures 4-125 through 4-128, all showed excellent agreement between the SCC and OC systems.

Figure 4-125. Comparison of flame temperature for ethanol fuel as a function of air stream/EGR temperature in SCC system and an equivalent unvitiated OC system at EGR = 0.0 and EGR = 2.0, \( \phi = 1.0 \), \( \tau_{res} = 10.0 \) ms.
Figure 4-126. Comparison of UHC emission index for ethanol fuel as a function of air stream/EGR temperature in SCC system and an equivalent unvi tiated OC system at EGR = 0.0 and EGR = 2.0, $\phi = 1.0$, $\tau_{\text{res}} = 10.0$ ms.

Figure 4-127. Comparison of CO emission index for ethanol fuel as a function of air stream/EGR temperature in SCC system and an equivalent unvi tiated OC system at EGR = 0.0 and EGR = 2.0, $\phi = 1.0$, $\tau_{\text{res}} = 10.0$ ms.
Figure 4-128. Comparison of OH emission index for ethanol fuel as a function of air stream/EGR temperature in SCC system and an equivalent unvi tiated OC system at EGR = 0.0 and EGR = 2.0, $\phi = 1.0$, $\tau_{res} = 10.0$ ms.
4.8 Case Study 7: Chemical Kinetic Sensitivity Analysis at the Blowout Limit for Ethanol Fuel

A sensitivity analysis study was carried out for ethanol fuel chemistry at the blowout limit. The results for cases of EGR = 0.0 and EGR = 2.0 have been presented in figures 4-130 and 4-131, respectively. The normalized OH sensitivity indices (defined by equation 4–26 [79]) for the most important reactions (indices greater than 1.0 for EGR of 0.0 and greater than 0.1 for EGR of 2.0) have been indicated. It was found that the normalized OH sensitivities were significantly lower at EGR = 2.0 than at EGR = 0.0. Clearly, the three reactions $O + OH = H + O_2$, $CO + OH = H + CO_2$ and $HCO = H + CO$ had the highest sensitivity indices at EGR of 0.0 and 2.0. Figure 4-49 depicts the change in blowout residence time for ethanol fuel, as a function of OH species mass fraction (See section 4.3 for details). For convenience, the predictions of blowout residence time at EGR=0.0 and EGR=2.0 has been shown in figure 4-129. From the figure, the curve fits for blowout residence time as a function of OH mass fraction were obtained, with a functional dependence given by $(\tau_{res})_{BO} = 202.86 \cdot \exp(-0.0075 \cdot y_{OH})$ and $(\tau_{res})_{BO} = 0.085 \cdot \exp(-0.0018 \cdot y_{OH})$ at EGR=0.0 and 2.0, respectively. These curve fit equations may further be differentiated to derive an expression for differential changes in blowout residence times $(d\tau_{res})_{BO} = -0.0075 \cdot dy_{OH}$ for EGR=0.0 and $(d\tau_{res})_{BO} = -0.0018 \cdot dy_{OH}$ for EGR=2.0. An expression for $dy_{OH}$ may thus be derived, given by $dy_{OH} = y_{OH} \cdot s_{i,OH}^{norm} \cdot \partial (ln k_i)$. The estimated percentage change in blowout residence times were found from equations 4–27 and 4–28 for EGR of 0.0 and 2.0, respectively. The values of $y_{OH}$ at $T_A = \text{EGRT} = 1000 \text{ K}$ were 0.00338775 (EGR=0.0) and 0.00118884 (EGR=2.0). The sensitivity indices of the blowout residence times (given by equation 4–29) for the most dominant reactions, have been summarized in table 4-1. It was found that these sensitivity indices were fairly low, indicating good reliability of the results.
Table 4-1. Sensitivity Analysis for blowout residence time

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$s_{i,OH}^{\text{norm}}$ (EGR=0.0)</th>
<th>$s_{i,OH}^{\text{norm}}$ (EGR=2.0)</th>
<th>$s_{\tau,i}^{\text{norm}}$ (EGR=0.0)</th>
<th>$s_{\tau,i}^{\text{norm}}$ (EGR=2.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O + OH = H + O_2$</td>
<td>53.1754</td>
<td>1.00407</td>
<td>0.00135</td>
<td>2.148e-6</td>
</tr>
<tr>
<td>$CO + OH = H + CO_2$</td>
<td>30.0605</td>
<td>0.320719</td>
<td>0.00076</td>
<td>6.863e-7</td>
</tr>
<tr>
<td>$HCO = H + CO$</td>
<td>27.2074</td>
<td>0.682872</td>
<td>0.00069</td>
<td>1.461e-6</td>
</tr>
</tbody>
</table>

\[ s_{ij}^{\text{norm}} = \frac{dy_j}{y_j} \frac{k_i}{dk_i} = \frac{d(\ln y_j)}{d(\ln k_i)} \]  \hspace{1cm} (4–26)

\[ \left( \frac{d\tau_{\text{res}}}{\tau_{\text{res}}} \right)_{BO} = -0.0075 \cdot y_{OH} \cdot s_{i,OH}^{\text{norm}} \cdot d(\ln k_i) ; \text{ (EGR}=0.0) \]  \hspace{1cm} (4–27)

\[ \left( \frac{d\tau_{\text{res}}}{\tau_{\text{res}}} \right)_{BO} = -0.0018 \cdot y_{OH} \cdot s_{i,OH}^{\text{norm}} \cdot d(\ln k_i) ; \text{ (EGR}=2.0) \]  \hspace{1cm} (4–28)

\[ s_{\tau,i}^{\text{norm}} = \frac{d(\ln \tau_{\text{res}})_{BO}}{d(\ln k_i)} \]  \hspace{1cm} (4–29)

Figure 4-129. Comparison of blowout residence time for ethanol fuel as a function of OH species mass fraction at EGR = 0.0 and 2.0, EGRT = 400, 600, 800, 1000, 1200 K, $\phi = 1.0$, $P = 202.65 \text{ kPa (2 atm)}$. 

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Figure 4-130. Normalized OH Sensitivity Indices before flame blowout at EGR = 0.0, $\phi = 1.0$, $T = 1000$ K.
Figure 4-131. Normalized OH Sensitivity Indices before Flame Blowout at EGR = 2.0, T$_\text{A}$, and $\varphi = 1.0, T\text{A} = 1000$ K.

Normalized OH Sensitivity Indices before Flame Blowout at EGR = 2.0.
CHAPTER 5
SUMMARY AND CONCLUSIONS

The flame blowout, combustion efficiency and pollutants generation (including CO, UHC, soot precursors and particulate soot) of various conventional and bio-derived fuels was investigated in vitiated and non-vitiated environment. The simulations were performed using a constant-pressure CSTR model developed using the Cantera combustion code, implemented in C++. The following general conclusions may be drawn from this study:

- The impact of fuel composition on combustion efficiency and flame temperature, is significantly dampened out with use of EGR. Hence, PoWER systems had superior fuel-flexibility characteristics compared to conventional open cycle systems.

- All biofuels tested had superior or comparable combustion efficiencies when compared to conventional fuels.

- The transition of flameless combustion in homogenous systems may be characterized based on critical temperature boundaries of soot formation, critical equivalence ratio, threshold values for soot precursors (PAH and acetylene) or OH emissions. In heterogenous combustion systems, flameless combustion transition may further be classified based on degree of homogeneity achieved.

- There is a significant drop in blowout limits of semiclosed systems with reduction in equivalence ratio, EGR T and pressure and, increase in EGR. The blowout limits were found to be a strong function of ignition number and, OH and CO emission indices. In addition it was found that the performance of semiclosed systems may be derived from equivalent open-cycle systems.

- The correlations of blowout loading parameters with ignition number, based on detailed chemical kinetics may be used to characterize the blowout, similar to loading parameter versus Damkohler number trends from global models for blowout.

- The primary effect of vitiation was found to be that of the increase in the residence time of the fresh reactant streams and temperature suppression, corresponding to increased levels of EGR (assuming that recirculation stream composition is the same as the exhaust composition).

The specific conclusions drawn from individual case studies have been summarized in the subsequent sections.
5.1 Case Study 1: Syngas and Methane Fuel Simulations

- The combustion performance (flame blowout, combustion efficiency and emissions) of three different mixtures of syngas given by, Syn75 (CO: 0.25, H$_2$: 0.75), Syn50 (CO: 0.5, H$_2$: 0.5) and Syn25 (CO: 0.75, H$_2$: 0.25), were analyzed. The results of the syngas mixtures were compared to that of Methane fuel, for varying levels of EGR and equivalence ratio. The effects of adiabatic and non-adiabatic EGR with temperature of 1200 K were compared. The simulations were performed at an air stream temperature of 400 K, equivalence ratio of 0.4, 0.6, 0.8, 1.0 (fuel-lean side) and 1.2, 1.6, 2.0 and 3.0 (fuel-rich side), EGR of 0.0, 1.0 and 2.0, pressure of 202.65 kPa (2.0 atm), and a residence time of 5 ms.

- The maximum temperature was found to occur under rich conditions for syngas mixtures and near equivalence ratio of unity for Methane. Methane fuel produced lower flame temperatures compared to all the syngas mixtures tested. Syn75 had highest temperatures at stoichiometric conditions or slightly lean conditions. At equivalence ratios away from stoichiometric on fuel-rich side, Syn75 exhibited lower flame temperatures, despite the higher H$_2$ content of the fuel. Typically, Syn25 had highest temperatures on the rich side as well as at very low equivalence ratios.

- The combustion efficiency was found to drop with rising equivalence ratios, for syngas mixtures. Increasing H$_2$ content of syngas fuel decreased combustion efficiency. Syn75 fuel had UHC emission indices comparable to that of methane until equivalence ratio of 1.2, beyond which he UHC emissions increased considerably for Methane fuel. Syn75 produced highest UHC emission indices followed by Syn50 and the lowest was that from Syn25.

- The combustion efficiency for all fuel mixtures, increased with accompanying decreases in UHC and CO emissions, with increasing adiabatic EGR. At fuel-rich conditions, the increase in efficiency was very low. The effect of increasing adiabatic EGR on UHC emissions was of lowering UHC for syngas combustion. The combustor temperatures approached equilibrium temperatures with increasing adiabatic EGR, for all equivalence ratios tested. The effect of EGR cooled to a temperature of 1200 K on the combustor flame temperature was of lowering the flame temperatures with increasing EGR. Trends in UHC and CO emissions for non-adiabatic EGR were the same as those for adiabatic EGR except for reduced flame stability.

- An increase in the blowout limits for adiabatic EGR, while a decrease in blowout limits at non-adiabatic EGR with temperature of 1200 K was observed. The extinction characteristics improved considerably with an increase in H$_2$ content.

- The soot concentrations were quantified by the concentration of the precursors of soot nuclei, the pyrene molecules (A$_4$ species). All syngas mixtures tested showed very low sooting tendency. With Methane fuel, significantly higher EI A$_4$ values were observed only at fuel-rich equivalence ratios greater than 1.6. It was observed that
the A4 emissions increased with an increase in adiabatic EGR at high equivalence ratios.

5.2 Case Study 2: Biofuels and n-Heptane Fuel Simulations

• The combustion performance of the biofuels ethanol, Dimethyl Ether (DME) and biodiesel surrogate Methyl Butanoate (MB) were modeled in a CSTR model, and compared against that of diesel fuel surrogate, n-heptane. A comparison has been presented of the flame blowout stability, combustion efficiency and emissions for equivalence ratios varying between 0.4 to 1.0 and exhaust gas recirculation (EGR) of 0.0, 1.0 and 2.0, with the recirculation stream cooled to temperature of 700 K. The emissions and combustion efficiency were compared at a residence time of 10.0 ms.

• The blowout temperature was found to drop with decreasing equivalence ratio for all fuels. The blowout simulation results had some inherent scatter in their trends due to the instabilities in computation.

• At an EGR of 0.0, MB had the highest blowout LP values indicating higher blowout stability over most blowout equivalence ratios, while ethanol and DME had lower blowout LP values, in comparison to n-heptane. At an EGR of 2.0, ethanol had the maximum blowout LP values, while n-heptane, MB and DME had comparable values.

• A considerable reduction in combustion blowout stability was found, with increase in EGR (for an EGR temperature of 700 K). The limits of operability in the range of equivalence ratio and flame temperature were considerably narrowed. This is an inherent drawback of the PoWER system that may be overcome by the utilization of fuels with wider blowout stability limits, such as hydrogen and syngas, using higher inlet stream temperatures or higher EGR temperatures, or possibly methods like H2 enrichment.

• For simulations performed at a residence time of 10.0 ms, the combustion efficiency increased with decreasing equivalence ratio in the range 0.4 to 1.0, for EGR of 0.0, while it was maximum at an optimum equivalence ratio of about 0.9 for EGR of 2.0. The equivalence ratios for minimum CO emissions were 0.5 and 0.9, for EGR of 0.0 and 2.0, respectively. The optimum equivalence ratio for minimum emissions and maximum combustion efficiency was found to shift towards stoichiometric, with increasing EGR. Hence, operating at a low equivalence ratio at high EGR, could result in reduction in combustion performance instead of improving it.

• All biofuels tested had superior or comparable combustion efficiencies compared to n-heptane.

• MB had generally higher combustion efficiency and substantially lower UHC, while CO emissions were reasonably low. Hence, use of MB in a PoWER system, had potential to substantially lower the overall pollutant emissions and improve
efficiency, since NO\textsubscript{x} emissions in PoWER system is low due to lower operating flame temperatures.

- The impact of fuel composition on combustion efficiency and flame temperature, is significantly dampened out with use of EGR. Hence, PoWER systems had superior fuel-flexibility characteristics compared to conventional open cycle systems.

### 5.3 Case Study 3: Study of EGR Temperature/EGR level on Ethanol Blowout Limits

- In this study, the blowout stability of ethanol fuel was investigated, in the regime of vitiated combustion. The test conditions were EGR = 0.0, 0.5, 1.0, 1.5, 2.0, \( T_A = \text{EGRT} = 400, 600, 800, 1000, 1200 \text{ K} \), \( \phi = 1.0 \) and \( P = 202.65 \text{ kPa} \) (2 atm).

- It was observed that the blowout temperature varied nearly linearly with EGR temperature, but non-linearly with EGR. A marked reduction in flame blowout stability was observed with increasing levels of EGR.

- The LP, residence time and total mass flow rate at blowout varied linearly on a logarithmic scale with EGR temperature, for various EGR levels.

- The normalized LP predictions (normalized to the corresponding results at EGR=0.0) were found to be a strong function of normalized temperatures, and OH and CO emissions at blowout.

- The approach may be potentially useful in making predictions of blowout stability margin, based on measurements of combustion efficiency. Moreover, the methodology of normalized predictions, if suitably applied, can be used to predict the blowout limits of SCC engines from the blowout predictions of conventional open cycle (OC) engines, potentially reducing the expense for extensive testing.

- The loading parameter was also found to correlate well with the ignition number.

### 5.4 Case Study 4: A Study of the Effect of EGR Temperature/EGR level/Residence Time/Equivalence Ratio on Soot Formation (Acetylene Fuel Combustion)

- Modeling studies were conducted in order to establish a correlation between flameless combustion attained through high levels of exhaust gas recirculation (EGR) in a Power, Water Extraction and Refrigeration (PoWER) engine and the process of soot formation. The gas phase chemistry for the soot formation process in the combustor primary zone has been modeled using a CSTR model. The CSTR pressure was \( P=202.65 \text{ kPa} \) (2.0 atm). Four cases were investigated in order to isolate the effects of various parameters:

1. case 1: EGR = 0.0-5.0, \( \phi = 2.0 \), \( \tau = 1.0 \), \( \text{EGRT}=1000 \text{ K} \)
2. case 2: \( EGRT = 400-1200 \text{ K}, \text{ EGR} = 0.0 \text{ and } 2.0, \phi = 2.0, \tau = 1.0 \)
3. case 3: \( \phi = 0.5-5.0, \text{ EGR} = 0.0 \text{ and } 2.0, \tau = 1.0, \text{ EGRT} = 1000 \text{ K} \)
4. case 4: \( \tau = 0.1-10.0, \phi = 2.0, \text{ EGR} = 0.0 \text{ and } 2.0, \text{ EGRT} = 1000 \text{ K} \)

- The emission indices for CO, UHC and soot precursors increase with EGR, while decrease with increasing EGR temperature.
- For the cases tested, while the open cycle (OC) case of zero EGR showed practically no soot precursor formation, the semi-closed cycle (SCC) cases depicted rising levels of soot formation with increasing EGR.
- EI UHC increased while EI CO and EI \( C_2H_2 \) decreased with EGR, before stabilizing to a constant value beyond EGR of about 3.0
- The combustion efficiency was found to decrease with EGR, after an initial slight increase.
- The PAH emission indices increased to a maximum at about EGR of 2.0, and then nearly linearly decreased with EGR.
- The EGR temperature (same as inlet air temperature) did not affect UHC, CO emissions for zero EGR case, while lowered EI UHC and EI \( C_2H_2 \), and increased CO emission indices slightly. The combustion efficiency was not affected for EGR=0.0, while combustion efficiency improved for EGR=2.0.
- EI for PAHs had a bell-shaped dependence with respect to EGR temperature, however, there was also a general decreasing trend at EGR of 0.0. The EI for PAHs were much higher at EGR=2.0 as compared with EGR=0.0.
- EI UHC and \( C_2H_2 \) increased with increasing equivalence ratio. However, a characteristic minimum existed depending on EGR and EGR temperature. The EI CO values increased for rich-side equivalence ratios to a maximum, and then nearly linearly decreased.
- The combustion efficiency decreased with equivalence ratio. The combustion efficiency for EGR=2.0 was significantly higher upto equivalence ratio of about 2.0.
- There was a sharp increase in EI \( C_2H_2 \) between equivalence ratios 1.0 and 2.0. The EI PAH trends were similar to the EI \( C_2H_2 \) trends.
- The residence time plots indicate that at EGR=0.0, high oxidative regime was dominant due to higher flame temperatures, while EGR=2.0, the temperatures were between 1400-2100 K, and hence EI PAH increased with residence time.
5.5 Case Study 5: Soot Particle Growth and Oxidation in Vitiated Combustion of Acetylene Fuel

In this study, the vitiated combustion of acetylene in a CSTR was modeled, in order to quantify the effect of vitiation on particulate soot formation. The conditions of simulation were $\phi = 2.0$, $P = 202.65$ kPa (2.0 atm), EGR = 0.0 and 2.0 and flame temperatures between 1500-2000 K.

- An increase in soot volume fraction and particle diameters with EGR was observed, although the soot growth processes of nucleation, coagulation and surface chemistry, were all suppressed.

- The primary effect of vitiation contributing to the increase in soot volume fraction was found to be that of the increase in the residence time of the fresh reactant streams, corresponding to increased levels of EGR.

5.6 Case Study 6: Modeling of Semi-Closed Cycle Engine Characteristics Using a Kinetically Equivalent Unvitiated Open-Cycle CSTR System

An approach was outlined on the use of an unvitiated OC system to model the combustion characteristics of an SCC system. Four cases of equivalent systems were analyzed, to determine an appropriate modeling approach. Simulations were run for $\phi = 1.0$, and $\tau_{res} = 10$ ms (for SCC system), EGRT = 600, 800, 1000 and 1200 K, EGR = 0.0 and 2.0. A very good agreement was found between theoretical modeling and simulation results.

- It may be concluded that the primary effect of EGR is simultaneous flame temperature reduction and increase in residence time of the fresh reactants, given the assumption that EGR stream composition is the same as that of the exhaust.

- For any given SCC system, a kinetically equivalent OC system may be determined that would match the exit state and therefore, blowout and/or emissions characteristics of the SCC system, if appropriate mass flow scaling was applied to the OC system.

5.7 Case Study 7: Chemical Kinetic Sensitivity Analysis at the Blowout Limit for Ethanol Fuel

A sensitivity analysis was performed on the effect of variation of rate constants on the species mass fractions at blowout. The OH mass fractions at blowout have been shown to correlate with the loading parameter. Therefore, a qualitative understanding of the sources
of the model uncertainties was from the sensitivity indices. The analysis was performed for the conditions of $\phi = 1.0$, EGR = 0.0 and 2.0, EGRT = 1000 K. The uncertainties in the blowout residence times from uncertainties in the reaction rates were found to be low. However, for exact quantitative correlations of the residence time (or loading parameter) variations with OH emissions, the published experimental uncertainties, on each of the reactions, need to be taken into account.

5.8 Proposed Future Studies

- To integrate Frenklach’s soot particulate growth model (including fractal aggregation submodel) into the detailed chemical kinetics model.

- To investigate flame stability at constant flame temperatures, using stabilization through heat flux across reactor wall.

- To compare effects of individual diluents ($\text{CO}_2$, $\text{H}_2\text{O}$, $\text{N}_2$) on combustion stability and soot formation, at fixed flame temperature.

- To study simultaneous optimization of gas cycle thermodynamics and emissions, and characterization of blowout limits for a practical system using reactor network for given combustor liner geometry.
APPENDIX A
GOVERNING EQUATIONS OF CSTR MODEL

A.1 Transient CSTR - Single Stream Model

The summary of CSTR model described in this section is based on [210, 211]. The general assumptions for the model are listed below:

- The system consists of single inlet and exit streams.
- The gases are assumed to be thermally ideal.
- Instantaneous mixing of products and reactants, $Da \rightarrow \infty$.
- The effects of species diffusion, conductivity and viscosity are absent.
- The system is chemically controlled.
- The reactor pressure is constant.
- The system is spatially homogenous.
- The system initial condition and inlet stream states are known.

For the simulations in cantera, further constraints were imposed as listed below.

- The system consists of multiple inlet and exit streams.
- The reactor wall velocity is zero.
- The reactor surface reactions do not occur.
- The changes in kinetic and potential energies through the system are negligible.

A.1.1 Reaction Kinetics of the Gas Mixture

A general reaction scheme for a reacting species pool $S_j$, is given as:

$$a_{ij}S_j \rightleftharpoons b_{ij}S_j$$

The species mass balance may be written as:

$$\sum_{i=1}^{n_R} \sum_{j=1}^{n_S} a_{ij} \dot{M}_j = \sum_{i=1}^{n_R} \sum_{j=1}^{n_S} b_{ij} \dot{M}_j$$  \hspace{1cm} (A–1)
\[ \sum_{i=1}^{n_R} \sum_{j=1}^{n_S} (b_{ij} - a_{ij}) \bar{M}_j = \sum_{i=1}^{n_R} \sum_{j=1}^{n_S} (\nu_{ij}) \bar{M}_j = 0 \quad (A-2) \]

For elemental mass balance, consider species \( S_j = (E_1)_{e_1} (E_2)_{e_2} \cdots (E_k)_{e_k} \).

The species molecular weight may be calculated as the sum of the mass contributions from each of the elements.

\[ \bar{M}_j = \sum_{k=1}^{n_k} \bar{M}_{E_k} e_{kj} \quad (A-3) \]

\[ \sum_{i=1}^{n_R} \sum_{j=1}^{n_S} \sum_{k=1}^{n_k} (\nu_{ij} e_{kj}) \bar{M}_{E_k} = 0 \quad (A-4) \]

which gives,

\[ \sum_{i=1}^{n_R} \sum_{j=1}^{n_S} (\nu_{ij} e_{kj}) = 0 \quad (A-5) \]

### A.1.1.1 Equilibrium constants

The equilibrium constant,

\[ k_{P,i} = \exp \left( -\frac{\Delta G^\circ}{\bar{R} u T} \right) = \prod_{j=1}^{n_S} \left( \frac{p_{j,eq}}{p^o} \right)^{\nu_{ij}} = \prod_{j=1}^{n_S} (c_{j,eq})^{\nu_{ij}} (\bar{R} u T)^{\nu_{ij}} \quad (A-6) \]

\[ k_{C,i} = \frac{k_{f,i}}{k_{b,i}} = \prod_{j=1}^{n_S} (c_{j,eq})^{\nu_{ij}} \quad (A-7) \]

\[ k_{P,i} = \exp \left( \frac{\Delta S^\circ}{\bar{R} u} - \frac{\Delta H^\circ}{\bar{R} u T} \right) = K_{C,i} (\bar{R} u T)^{\left( \sum_{j=1}^{n_S} \nu_{ij} \right)} \quad (A-8) \]

### A.1.1.2 Rate of reaction

The forward rate coefficient is given by:

\[ k_{f,i} = A_i T^b e^{-\frac{E_i}{\bar{R} u T}} \quad (A-9) \]
The rate of a reaction $i$ is given as:

$$\dot{r}_i \equiv \frac{1}{V} \frac{d\epsilon}{dt} = \frac{1}{V} \frac{dn_{ij}}{dt} \quad (A-10)$$

$$\dot{r}_i = k_{f,i} (T) \prod_{j=1}^{n_S} (c_j)^{b_{ij}} - k_{b,i} (T) \prod_{j=1}^{n_S} (c_j)^{a_{ij}} \quad (A-11)$$

$$\dot{r}_i = A_i T^b e^{\frac{E}{RT}} (T) \prod_{j=1}^{n_S} (c_j)^{a_{ij}} \left[ 1 - \frac{1}{K_{C,i} (T)} \prod_{j=1}^{n_S} (c_j)^{\nu_{ij}} \right] \quad (A-12)$$

### A.1.1.3 Species production rate

The rate of a reaction $i$ is given as:

$$\dot{\omega}_j \equiv \frac{1}{V} \frac{dn_j}{dt} = \frac{1}{V} \frac{\sum_{i=1}^{n_R} dn_{ij}}{dt} = \frac{1}{V} \sum_{i=1}^{n_R} \nu_{ij} \dot{r}_i \quad (A-13)$$

### A.1.2 Species Conservation

\[(Accumulation) = (Inflow) - (Outflow) + (Generation) \quad (A-14)\]

### A.1.2.1 Mass basis

\[
\left( \frac{dm_j}{dt} \right)_{CV} = (\dot{m}_{j, in} - \dot{m}_{j, ex}) + (\bar{M}_j \cdot V_R \cdot \dot{\omega}_j) + \dot{m}_{j, int}
\]

\[
= (\dot{m}_{in} y_{j, in} - \dot{m}_{ex} y_{j, ex}) + (\bar{M}_j V_R \dot{\omega}_j) + \dot{m}_{j, int} \quad (A-15)
\]

$$\dot{m}_{ex} = K_V \Delta P \quad (A-16)$$

$$m_{j, int} = \bar{M}_j A_R \dot{s}_j \quad (A-17)$$
A.1.2.2 Molar basis

\[
\left( \frac{dn_j}{dt} \right)_{CV} = (\dot{n}_{j,\text{in}} - \dot{n}_{j,\text{ex}}) + (V_R \dot{\omega}_j) + \dot{n}_{j,\text{int}}
\]

\[= (\dot{n}_{in} x_j, \text{in} - \dot{n}_{ex} x_j, \text{ex}) + (V_R \dot{\omega}_j) + \dot{n}_{j,\text{int}} \quad (A-18) \]

\[\dot{n}_{j,\text{int}} = A_R \dot{s}_j \quad (A-19) \]

A.1.2.3 Concentration basis

\[
\left( \frac{dn_j}{dt} \right)_{CV} = (\dot{\hat{Q}}_{c,j,\text{in}} - \dot{\hat{Q}}_{c,j,\text{ex}}) + (V_R \dot{\omega}_j) + \dot{n}_{j,\text{int}} 
\]

\[= (\dot{\hat{Q}}_{c,j,\text{in}} - \dot{\hat{Q}}_{c,j,\text{ex}}) + (V_R \dot{\omega}_j) + \dot{n}_{j,\text{int}} \quad (A-20) \]

A.1.3 Conservation of Total Mass

A.1.3.1 Mass basis

\[
\left( \frac{dm}{dt} \right)_{CV} = (\dot{m}_{\text{in}} - \dot{m}_{\text{ex}}) + (\dot{m}_{\text{gen}}) + \dot{m}_{\text{int}} 
\]

\[= (\dot{m}_{\text{in}} - \dot{m}_{\text{ex}}) + (\dot{m}_{\text{gen}}) + \dot{m}_{\text{int}} \quad (A-21) \]

\[\dot{m}_{\text{gen}} = V_R \sum_{j=1}^{n_S} \bar{M}_j \dot{\omega}_j = V_R \sum_{i=1}^{n_S} \sum_{j=1}^{n_S} n_j (\nu_{ij} \ddot{r}_i) = 0 \quad (A-22) \]

\[V_R \sum_{i=1}^{n_S} (\bar{M}_j \nu_{ij}) = 0 \quad (A-23) \]

\[
\left( \frac{dm}{dt} \right)_{CV} = (\dot{\hat{Q}}_{\rho,\text{g, in}} - \dot{\hat{Q}}_{\rho,\text{g, ex}}) + (\dot{m}_{\text{gen}}) + \sum_j \dot{m}_{j,\text{int}} 
\]

\[= (\dot{\hat{Q}}_{\rho,\text{g, in}} - \dot{\hat{Q}}_{\rho,\text{g, ex}}) + (\dot{m}_{\text{gen}}) + \sum_j \dot{m}_{j,\text{int}} \quad (A-24) \]

A.1.3.2 Molar basis

\[
\left( \frac{dn}{dt} \right)_{CV} = (\dot{n}_{\text{in}} - \dot{n}_{\text{ex}}) + (\dot{n}_{\text{gen}}) + \dot{n}_{\text{int}} 
\]

\[= (\dot{n}_{\text{in}} - \dot{n}_{\text{ex}}) + (\dot{n}_{\text{gen}}) + \dot{n}_{\text{int}} \quad (A-25) \]

where,
\[(\dot{n}_{\text{gen}}) = \sum_{j=0}^{n_S} \dot{n}_{\text{gen},j} = \sum_{j=0}^{n_S} V_R \dot{\omega}_j = V_R \sum_{j=0}^{n_S} \sum_{i=0}^{n_R} \nu_{ij} \dot{r}_i = \sum_{i=0}^{n_R} \nu_{i, R} \dot{r}_i \quad (A-26)\]

\[\nu_{i, R} = \sum_{j=0}^{n_S} \nu_{ij} \quad (A-27)\]

\[\left(\frac{dn}{dt}\right)_{CV} = \left(\dot{Q}_{\text{in}} c^g_{\text{in}} - \dot{Q}_{\text{ex}} c^g_{\text{ex}}\right) + (V_R \dot{c}^g_{\text{gen}}) + V_R \dot{c}^g_{\text{int}} \quad (A-28)\]

### A.1.4 Conservation of Energy

\[(\text{Accumulation}) = (\text{Inflow}) - (\text{Outflow}) + (\text{Generation}) \quad (A-29)\]

#### A.1.4.1 Mass basis

\[\left(\frac{dE}{dt}\right)_{CV} = \left(\dot{E}_{\text{in}} - \dot{E}_{\text{ex}}\right) + A_R \dot{Q}_{\text{int}} - \left(\dot{W}\right) \quad (A-30)\]

\[\left(\frac{m_R \cdot e}{dt}\right)_{CV} = \left(\dot{m}_{\text{in}} e_{\text{in}} - \dot{m}_{\text{ex}} e_{\text{ex}}\right) + A_R \dot{Q}_{\text{int}} - \left(\dot{W}\right) \quad (A-31)\]

\[\dot{W} = P \frac{dV_R}{dt} + \dot{W}_s + \left(\frac{P}{\rho}\right)_{\text{ex}} \dot{m} - \left(\frac{P}{\rho}\right)_{\text{in}} \quad (A-32)\]

\[e = u + e_{KE} + e_{PE} = u + \frac{1}{2} v^2 + gz \quad (A-33)\]

\[\left(\frac{m_R (u + \frac{1}{2} v^2 + gz)}{dt}\right)_{CV} = \dot{m}_{\text{in}} \left(\left(u + \frac{1}{2} v^2 + gz\right)_{\text{in}} \right) - \dot{m}_{\text{ex}} \left(\left(u + \frac{1}{2} v^2 + gz\right)_{\text{ex}} \right) + A_R \dot{Q}_{\text{int}} - \left(P \frac{dV_R}{dt} + \dot{W}_s + \left(\frac{P}{\rho}\right)_{\text{ex}} \dot{m} - \left(\frac{P}{\rho}\right)_{\text{in}}\right) \quad (A-34)\]

Since, energy cannot be generated or destroyed, there is no explicit generation term for energy. However, there is energy conversion, inside the reactor, that acts like a source.
term even at steady state. This source term is part of the control-volume accumulation term in the above equation.

\[
\left( \frac{m_R \left( u + \frac{1}{2} v^2 + g z \right)}{dt} \right)_{CV} = \dot{m}_{in} \left( h + \frac{1}{2} v^2 + g z \right)_{in} - \dot{m}_{ex} \left( h + \frac{1}{2} v^2 + g z \right)_{ex} + A_R \dot{Q}_{int} - \left( P \frac{dV_R}{dt} + \dot{W}_s \right)
\]

\[
\left( \frac{\rho V_R \left( u + \frac{1}{2} v^2 + g z \right)}{dt} \right)_{CV} = \left( \frac{\rho V_R (u)}{dt} \right)_{CV}
\]

\[
= \left( \frac{\rho V_R (h - P/\rho)}{dt} \right)_{CV} = \left( \frac{\rho V_R (h)}{dt} \right)_{CV} - \left( P \frac{dV_R}{dt} + V_R \frac{dP}{dt} \right)_{CV}
\]

\[
\left( \frac{\rho V_R (h)}{dt} \right)_{CV} - \left( P \frac{dV_R}{dt} + V_R \frac{dP}{dt} \right)_{CV} = \dot{m}_{in} \left( h + \frac{1}{2} v^2 + g z \right)_{in} - \dot{m}_{ex} \left( h + \frac{1}{2} v^2 + g z \right)_{ex} + A_R \dot{Q}_{int} - \left( P \frac{dV_R}{dt} + \dot{W}_s \right)
\]

Assuming a thermally ideal gas mixture,

\[
P V_R = \sum_{j=1}^{n_g} n_j R_u T = n_g R_u T
\]

\[
\frac{1}{P} \frac{dP}{dt} + \frac{1}{V_R} \frac{dV_R}{dt} = \frac{1}{n_g} \frac{dn_g}{dt} + \frac{1}{T} \frac{dT}{dt}
\]

\[
\frac{dP}{dt} = P \left( \frac{1}{n_g} \frac{dn_g}{dt} + \frac{1}{T} \frac{dT}{dt} - \frac{1}{V_R} \frac{dV_R}{dt} \right)
\]
\[
\left( \frac{\rho V_R(h)}{dt} \right)_{CV} - \left( V_R P \left( \frac{1}{n_g} \frac{dn_g}{dt} + \frac{1}{T} \frac{dT}{dt} - \frac{1}{V_R} \frac{dV_R}{dt} \right) \right)_{CV} = \\
\dot{m}_{in} \left( h + \frac{1}{2} v^2 + gz \right)_{in} - \dot{m}_{ex} \left( h + \frac{1}{2} v^2 + gz \right)_{ex} + V_R \dot{Q}_{int} - \dot{W}_s \tag{A-41}
\]

Note that for the special case of zero wall-velocity, the term \( \frac{dV_R}{dt} \) is zero.

Since the gases have been assumed to be calorically non-ideal,

\[
h = h(T) = \sum_{j=0}^{n_S} Y_j \left( h_{f,j}^o + \int_{T_{ref}}^{T} c_{P,j}(T) \, dT \right) \tag{A-42}
\]

where \( h(T) \) are given be NASA parametrized polynomials. See Appendix [B].

From Kinetics,

\[
\frac{dn_j}{dt} = (\dot{n}_{j, \text{in}} - \dot{n}_{j, \text{ex}}) + V_R \dot{\omega}_j \tag{A-43}
\]

\[
\left( \frac{dm_j}{dt} \right)_{CV} = (\dot{m}_{j, \text{in}} - \dot{m}_{j, \text{ex}}) + V_R M_j \dot{\omega}_j \tag{A-44}
\]

We could assume that we reach the state of products by sensibly heating the reactants to the exit temperature and then allowing for the reaction to take place at that temperature. To accomplish this, we could multiply the species conservation equation with \( h_j(T_{ex}) \) to get,

\[
\sum_{j=0}^{n_S} h_j(T_{ex}) \frac{dm_j}{dt} = \sum_{j=0}^{n_S} h_j(T_{ex}) (\dot{m}_{j, \text{in}} - \dot{m}_{j, \text{ex}}) + \sum_{j=0}^{n_S} V_R h_j(T_{ex}) M_j \dot{\omega}_j \tag{A-45}
\]

Note that the term \( \bar{h}_j(T) M_j \dot{\omega}_j \) can be written as,
\[ \tilde{h}_j(T_{ex}) \dot{M}_j \dot{\omega}_j = V_R \sum_{j=0}^{n_S} \sum_{i=0}^{n_R} \tilde{M}_j \tilde{h}_j(T_{ex}) (\nu_{ij} \dot{r}_i) = V_R \sum_{i=0}^{n_R} \Delta H_{\text{rxn},i} \dot{r}_i = V_R \sum_{i=0}^{n_R} \Delta H_{\text{rxn},i} \dot{r}_i = V_R \dot{Q}_{\text{gen},g} \]

(A–46)

where \( \Delta \tilde{H}_{\text{rxn},i}(T) = \sum_{j=0}^{n_S} \tilde{h}_j \nu_{ij} \)

Subtracting equation (A–46) from (A–41) gives,

\[
\sum_{j=0}^{n_S} \left( m_j \left( \frac{dh_j(T)}{dt} \right) \right)_{CV} - \left[ V_R P \left( \frac{1}{n_g} \frac{dn_g}{dt} + \frac{1}{T} \frac{dT}{dt} - \frac{1}{V_R} \frac{dV_R}{dt} \right) \right]_{CV} = \\
\sum_{j=0}^{n_S} \dot{m}_{j, \text{in}} \left( \frac{1}{2} \rho v^2 + gz \right)_{\text{in}} - \sum_{j=0}^{n_S} \dot{m}_{j, \text{ex}} \left( \frac{1}{2} \rho v^2 + gz \right)_{\text{ex}} + (V_R \dot{Q}_{\text{gen},g}) + A_R \dot{Q}_{\text{int}} \\
- \left( \dot{W}_s \right) + \sum_{j=0}^{n_S} \dot{m}_{j, \text{in}} [h_j(T_{\text{in}}) - h_j(T_{\text{ex}})] + \dot{m}_{j, \text{ex}} [h_j(T_{\text{ex}}) - h_j(T_{\text{ex}})] \quad (A–47)
\]

A.1.4.2 Molar basis

\[
\left( \frac{n_g (\bar{h}_g)}{dt} \right)_{CV} - \left[ V_R P \left( \frac{1}{n_g} \frac{dn_g}{dt} + \frac{1}{T} \frac{dT}{dt} - \frac{1}{V_R} \frac{dV_R}{dt} \right) \right]_{CV} = \\
\dot{n}_{g, \text{in}} \left( \bar{h} + \frac{1}{2} M_g \rho v^2 + \frac{1}{M_g} gz \right)_{\text{in}} - \dot{n}_{g, \text{ex}} \left( \bar{h} + \frac{1}{2} M_g \rho v^2 + \frac{1}{M_g} gz \right)_{\text{ex}} + A_R \dot{Q}_{\text{int}} - \left( \dot{W}_s \right) \quad (A–48)
\]

From Kinetics,

\[
\frac{dn_j}{dt} = (\dot{n}_{j, \text{in}} - \dot{n}_{j, \text{ex}}) + V_R \dot{\omega}_j \quad (A–49)
\]

Multiplying the above equation with \( \tilde{h}_j(T_{\text{ex}}) \), gives,

\[
\sum_{j=0}^{n_S} \tilde{h}_j(T_{\text{ex}}) \frac{dn_j}{dt} = \sum_{j=0}^{n_S} \tilde{h}_j(T_{\text{ex}}) (\dot{n}_{j, \text{in}} - \dot{n}_{j, \text{ex}}) + \sum_{j=0}^{n_S} V_R \tilde{h}_j(T_{\text{ex}}) \dot{\omega}_j \quad (A–50)
\]

Note that the term \( \tilde{h}_j(T) \dot{\omega}_j \) can be written as,
\[
\bar{h}_j (T_{ex}) \dot{\omega}_j = V_R \sum_{j=0}^{n_S} \sum_{i=0}^{n_R} \bar{h}_j (T_{ex}) (\nu_{ij} \dot{r}_i) = V_R \sum_{i=0}^{n_R} \Delta H_{rxn, i} \dot{r}_i = V_R \dot{Q}_{gen, g} \quad (A-51)
\]

where \(\Delta H_{rxn, i} (T) = \sum_{j=0}^{n_S} \bar{h}_j \nu_{ij}\)

Subtracting equation (A–51) from (A–48) gives,

\[
\begin{align*}
\sum_{j=0}^{n_S} \left( n_j \left( \frac{d h_j (T)}{dt} \right) \right)_{CV} &= \left[ V_R P \left( \frac{1}{n_g} \frac{dn_g}{dt} + \frac{1}{T} \frac{d T}{dt} - \frac{1}{V_R} \frac{d V_R}{dt} \right) \right]_{CV} = \\
\sum_{j=0}^{n_S} \dot{n}_{j, in} \left( \frac{1}{2} M_g \dot{\rho} v^2 + \frac{1}{M_g} g z \right)_{in} - \sum_{j=0}^{n_S} \dot{n}_{j, ex} \left( \frac{1}{2} M_g \dot{\rho} v^2 + \frac{1}{M_g} g z \right)_{ex} - (V_R \dot{Q}_{gen, g}) + A_R \dot{Q}_{int} \\
&- (\dot{W}_s) + \sum_{j=0}^{n_S} \dot{n}_{j, in} [\bar{h}_j (T_{in}) - \bar{h}_j (T_{ex})] + \dot{n}_{j, ex} [\bar{h}_j (T_{ex}) - \bar{h}_j (T_{ex})] \quad (A-52)
\end{align*}
\]

A.2 Transient CSTR - Multi-stream Model

A.2.1 Species Conservation

A.2.1.1 Mass basis

\[
\begin{align*}
\frac{dm_j}{dt}_{CV} &= \left( \sum_{s=1}^{N_{in}} \dot{m}_{in,s,j} - \sum_{s=1}^{N_{ex}} \dot{m}_{ex,s,j} \right) + (\dot{m}_{gen,j}) + \dot{m}_{int,j} \\
\frac{d (\rho V_R Y_j)}{dt}_{CV} &= \left( \sum_{s=1}^{N_{in}} \dot{m}_{s,in} Y_{s,j} - \sum_{s=1}^{N_{ex}} \dot{m}_{s,ex} Y_{s,j} \right) + (\dot{m}_{gen,j}) + \dot{m}_{int,j} \\
\frac{d (\rho V_R)}{dt}_{CV} &= \left( \sum_{s=1}^{N_{in}} \dot{Q}_{s,in} \rho_j - \sum_{s=1}^{N_{ex}} \dot{Q}_{s,ex} \rho_j \right) + (\dot{m}_{gen}) + \dot{m}_{int,j}
\end{align*}
\]

A.2.1.2 Molar basis

\[
\begin{align*}
\frac{dn_j}{dt}_{CV} &= \left( \sum_{s=1}^{N_{in}} \dot{n}_{in,s,j} - \sum_{s=1}^{N_{ex}} \dot{n}_{ex,s,j} \right) + (\dot{n}_{gen,j}) + \dot{n}_{int,j}
\end{align*}
\]
\[
\left( \frac{dn_j}{dt} \right)_{CV} = \left( \sum_{s=1}^{N_{in}} n_{in,s} x_{s,j} - \sum_{s=1}^{N_{ex}} n_{ex,s} x_{s,j} \right) + (\dot{n}_{gen,j}) + \dot{n}_{int,j} \tag{A-57}
\]

\[
\left( \frac{d(c_j V_R)}{dt} \right)_{CV} = \left( \sum_{s=1}^{N_{in}} \dot{Q}_{in,s} c_{s,j} - \sum_{s=1}^{N_{ex}} \dot{Q}_{ex,s} c_{s,j} \right) + (V_R \dot{\omega}_j) + \dot{n}_{int,j} \tag{A-58}
\]

### A.2.2 Conservation of Total Mass

#### A.2.2.1 Mass basis

\[
\left( \frac{dm}{dt} \right)_{CV} = \left( \sum_{s=1}^{N_{in}} \dot{m}_{s,in} - \sum_{s=1}^{N_{ex}} \dot{m}_{s,ex} \right) + (\dot{m}_{gen}) + \dot{m}_{int,j} \tag{A-59}
\]

\[
\dot{m}_{gen} = V_R \sum_{j=1}^{n_S} \bar{M}_j \dot{\omega}_j = V_R \sum_{i=1}^{n_S} \sum_{j=1}^{n_S} n_j (\nu_{ij} r_i) = 0 \tag{A-60}
\]

\[
V_R \sum_{i=1}^{n_S} (\bar{M}_j \nu_{ij}) = 0 \tag{A-61}
\]

\[
\left( \frac{d(\rho V_R)}{dt} \right)_{CV} = \left( \sum_{s=1}^{N_{in}} \dot{Q}_{s,in} \rho_{in,s,g} - \sum_{s=1}^{N_{ex}} \dot{Q}_{s,ex} \rho_{ex,s,g} \right) + (\dot{m}_{gen}) + \dot{m}_{int,j} \tag{A-62}
\]

#### A.2.2.2 Molar basis

\[
\left( \frac{dn}{dt} \right)_{CV} = \left( \sum_{s=1}^{N_{in}} \dot{n}_{in,s} - \sum_{s=1}^{N_{ex}} \dot{n}_{ex,s} \right) + (\dot{n}_{gen}) + \dot{n}_{int} \tag{A-63}
\]

where,

\[
(\dot{n}_{gen,g}) = \sum_{j=1}^{n_S} \dot{n}_{gen,j} = \sum_{j=1}^{n_S} V_R \dot{\omega}_j = V_R \sum_{j=1}^{n_S} \nu_{ij} \dot{r}_i = \sum_{i=1}^{n_R} \nu_{i,R} \dot{r}_i \tag{A-64}
\]

\[
\nu_{i,R} = \sum_{j=0}^{n_S} \nu_{ij} \tag{A-65}
\]

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\[
\left( \frac{d \left( c_g V_R \right)}{dt} \right)_{CV} = \left( \sum_{s=1}^{N_{in}} \dot{Q}_{in,s} c_{in,g,s} - \sum_{s=1}^{N_{ex}} \dot{Q}_{ex,s} c_{ex,g,s} \right) + \left( V_R \dot{c}_{gen,g} \right) + V_R \dot{c}_{int,g} \quad (A-66)
\]

A.2.3 Conservation of Energy

A.2.3.1 Mass basis

\[
\sum_{j=1}^{n_S} \left( \frac{m_j \left( dh_j(T) \right)}{dt} \right)_{CV} - \left[ V_R P \left( \frac{1}{n_g} \frac{dn_g}{dt} + \frac{1}{T} \frac{dT}{dt} - \frac{1}{V_R} \frac{dV_R}{dt} \right) \right]_{CV} = \\
\sum_{s=1}^{N_{in}} \sum_{j=1}^{n_S} \dot{m}_{in,s,j} \left( \frac{1}{2} \rho v^2 + gz \right)_{in} - \sum_{s=1}^{N_{ex}} \sum_{j=1}^{n_S} \dot{m}_{ex,s,j} \left( \frac{1}{2} \rho v^2 + gz \right)_{ex} + \left( V_R \dot{Q}_{gen,g} \right) + A_R \dot{Q}_{int} \\
- \left( \dot{W}_s \right) + \sum_{s=1}^{N_{in}} \sum_{j=1}^{n_S} \dot{m}_{in,s,j} \left[ h_j(T_{in}) - h_j(T_{ex}) \right] + \sum_{s=1}^{N_{ex}} \sum_{j=1}^{n_S} \dot{m}_{ex,s,j} \left[ h_j(T_{ex}) - h_j(T_{ex}) \right] \quad (A-67)
\]

A.2.3.2 Molar basis

\[
\sum_{j=0}^{n_S} \left( \frac{n_j \left( dh_j(T) \right)}{dt} \right)_{CV} - \left[ V_R P \left( \frac{1}{n_g} \frac{dn_g}{dt} + \frac{1}{T} \frac{dT}{dt} - \frac{1}{V_R} \frac{dV_R}{dt} \right) \right]_{CV} = \\
\sum_{j=1}^{n_S} \sum_{j=1}^{n_S} \dot{n}_{in,s,j} \left( \frac{1}{2} \frac{1}{M_g} \rho v^2 + \frac{1}{M_g} gz \right)_{in} - \sum_{j=1}^{n_S} \sum_{j=1}^{n_S} \dot{n}_{ex,s,j} \left( \frac{1}{2} \frac{1}{M_g} \rho v^2 + \frac{1}{M_g} gz \right)_{ex} + \left( V_R \dot{Q}_{gen,g} \right) + A_R \dot{Q}_{int} \\
- \left( \dot{W}_s \right) + \sum_{j=1}^{n_S} \sum_{j=1}^{n_S} \dot{n}_{in,s,j} \left[ \bar{h}_j(T_{in}) - \bar{h}_j(T_{ex}) \right] + \sum_{j=1}^{n_S} \sum_{j=0}^{n_S} \dot{n}_{ex,s,j} \left[ \bar{h}_j(T_{ex}) - \bar{h}_j(T_{ex}) \right] \quad (A-68)
\]
APPENDIX B
THERMODYNAMIC PROPERTIES OF GAS MIXTURES

This section describes the parametrization and derivation of thermodynamic
properties [210] for various species in a chemical kinetic mechanism.

B.1 Specific Heats

B.1.1 Calorically Ideal Gases

For a calorically ideal gas,

\[ \bar{C}_P^o (T) = \bar{C}_P^o (T_{ref}) \]  (B–1)

B.1.2 Calorically Non-Ideal Gases

For calorically non-ideal Gases,

- NASA polynomial

\[ \bar{C}_P^o = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 \]  (B–2)

- Shomate polynomial

\[ \bar{C}_P^o = a + b T + c T^2 + d T^3 + \frac{e}{T^2} \]  (B–3)

B.2 Enthalpy

\[ \bar{h}_j^o (T) = \bar{h}_j^o (T_{ref}) + \int_{T_{ref}}^{T} \bar{c}_P^o (T) \, dT \]  (B–4)

B.2.1 Constant \( C_P \) Parametrization

\[ \bar{h}_j^o (T) = \bar{h}_j^o (T_{ref}) + \bar{C}_P^o (T - T_{ref}) \]  (B–5)

B.2.2 NASA Parametrization

\[ \frac{\bar{h}_j^o (T)}{R_u T} = a_0 + \frac{a_1}{2} T + \frac{a_2}{3} T^2 + \frac{a_3}{4} T^3 + \frac{a_4}{5} T^4 + \frac{a_5}{T} \]  (B–6)
B.2.3 Shomate Parametrization

\[
\frac{\bar{h}^o_j(T)}{R_u T} = a + \frac{b}{2} T + \frac{c}{3} T^2 + \frac{d}{4} T^3 - \frac{e}{T^2} + f \tag{B–7}
\]

B.3 Entropy

From first law of thermodynamics,

\[TdS = dh - \nu dP \tag{B–8}\]

\[
\int_{s^o_j(T_{ref}, P^o)}^{\bar{s}_j(T, P)} d\bar{s}_j = \int_{T_{ref}}^{T} \frac{\rho^o_{P,j}(T)}{T} dT - \int_{P^o}^{P} \frac{R_u T}{P} dP \tag{B–9}\]

\[
\bar{s}_j(T, P) - \bar{s}^o_j(T_{ref}, P^o) = \int_{T_{ref}}^{T} \frac{\rho^o_{P,j}(T)}{T} dT - R_u T \ln \left( \frac{P}{P^o} \right) \tag{B–10}\]

\[
s^o_j(T, P^o) = s^o_j(T_{ref}, P^o) + \int_{T_{ref}}^{T} \frac{\rho^o_{P,j}(T)}{T} dT \tag{B–11}\]

\[
\bar{s}_j(T, P) = \bar{s}^o_j(T, P^o) - R_u T \ln \left( \frac{P}{P^o} \right) \tag{B–12}\]

B.3.1 Constant C\textsubscript{P} Parametrization

\[
\bar{s}^o_j(T) = \bar{s}^o_j(T_{ref}) + \rho^o_{P,j, ref} \ln \left( \frac{T}{T_{ref}} \right) \tag{B–13}\]

B.3.2 NASA Parametrization

\[
\frac{\bar{s}^o_j(T)}{R_u} = a_0 \ln(T) + a_1 T + \frac{a_2}{2} T^2 + \frac{a_3}{3} T^3 + \frac{a_4}{4} T^4 + a_6 \tag{B–14}\]

B.3.3 Shomate Parametrization

\[
\frac{\bar{s}^o_j(T)}{R_u} = a \ln(T) + b T + \frac{c}{2} T^2 + \frac{d}{3} T^3 - \frac{e}{2 T^2} + g \tag{B–15}\]
This section presents a summary of statistics applied in determination of moments for particle size distribution of aerosols [149, 221].

### C.1 Basic Statistics

**Probability distribution function** The probability distribution function \( F_P(x) \) represents the probability of \( x \) less than a number \( a \).

\[
F_P(x) = P(x < a) = \int_{-\infty}^{a} p(y)dy \quad (C-1)
\]

**Probability density function** The probability density function \( p(x) \) represents the probability of \( x \) less than a number \( a \).

\[
p(x) = \frac{dF_p}{dx} = \lim_{\Delta x \to 0} \frac{F_p[x + \Delta x] - F_p[x]}{\Delta x} \quad (C-2)
\]

**Moments of a variable** The \( r^{th} \) moment of a function is defined by:

\[
M_r = E[x^r] = \int_{-\infty}^{\infty} x^r p(x)dx \quad (C-3)
\]

\[
E[x^0] = \int_{-\infty}^{\infty} x^0 p(x)dx = 1 \quad (C-4)
\]

**Mean:**

\[
\mu_x = E[x^1] = \int_{-\infty}^{\infty} x^1 p(x)dx \quad (C-5)
\]

**Mean Square value:**

\[
\psi_x^2 = E[x^2] = \int_{-\infty}^{\infty} x^2 p(x)dx \quad (C-6)
\]

**Central Moments of a variable** The \( r^{th} \) central moment of a variable \( x \) is defined by:
\[ M_{C_r} = E[(x - \mu_x)^r] = \int_{-\infty}^{\infty} (x - \mu_x)^r p(x) dx \quad (C-7) \]

\[ M_{C_0} = E[(x - \mu_x)^0] = \int_{-\infty}^{\infty} (x - \mu_x)^0 p(x) dx = 1 \quad (C-8) \]

\[ M_{C_1} = E[(x - \mu_x)^1] = \int_{-\infty}^{\infty} (x - \mu_x)^1 p(x) dx = \mu_x - \mu_x = 0 \quad (C-9) \]

Variance:

\[ \sigma_x^2 = M_{C_2} = E[(x - \mu_x)^1] = \int_{-\infty}^{\infty} (x - \mu_x)^2 p(x) dx = \psi_x^2 - \mu_x^2 \quad (C-10) \]

Skewness:

\[ Skewness = \frac{M_{C_3}}{\sigma^3} \quad (C-11) \]

Kurtosis:

\[ Skewness = \frac{M_{C_4}}{\sigma^4} \quad (C-12) \]

Super-Skewness:

\[ Super - Skewness = \frac{M_{C_5}}{\sigma^5} \quad (C-13) \]

### C.2 Lagrangian Interpolation

The general \( n^{th} \) order interpolation at point \( x \) between grid points \( x_i \) for known \( y_i = y(x_i) \) is given by:

\[ P_n(x) = \sum_{i=1}^{n} l_i(x)y_i \quad (C-14) \]
$$l_i(x) = \prod_{j=1 \ (j \neq i)}^{n} \frac{x - x_j}{x_i - x_j} \quad \text{(C-15)}$$

$$\log(\mu_p) = P_n(p) = \sum_{i=1}^{n} l_i(p) \left[ \log(\mu_i) \right] \quad \text{(C-16)}$$

$$\mu_p = 10^{P_n(p)} = \prod_{i=1}^{n} [\mu_i]^{l_i(p)} \quad \text{(C-17)}$$
REFERENCES


BIOGRAPHICAL SKETCH

Bhupinder Singh was born in 1979, in the city Baroda, India, where he spent most of his life. He graduated with a Bachelor of Science in mechanical engineering in 2001 from Sardar Patel University, Gujarat, India. He joined Alstom India as an engineering trainee in 2001 and continued to work as a lead engineer until 2004. In 2004, he joined the University of Florida to pursue a PhD in mechanical engineering. He has been pursuing his research in the area of combustion, more specifically, on modeling of emissions, soot formation and flame blowout during vitiated combustion, in the PoWER engine. Broadly, his research interests are biofuels, flame blowout, flameless combustion, combustion kinetics and soot formation.