The high temperature heat extraction from a porous media reciprocal flow burner (RFB) is studied numerically. In RFB, the air/fuel mixture flow direction is switched periodically to contain and sustain combustion. High temperature heat extraction is essential for the efficient operation of small electrical and thermal systems based on thermoelectric generators, Stirling engines and micro-turbines. In this thesis, the efficiency of the heat extraction is studied for different extraction locations, temperatures and equivalence ratios. An 1-D time-averaged model is developed and validated to represent a RFB and to further predict the behavior of the burner. The results show that extraction from the lateral zone has a much higher efficiency than extraction from the central zone. When heat is extracted from the central zone, the efficiency decreases with the extraction temperature ($T_e$) and the equivalence ratio ($\phi$), changing from 6% to 2%. When heat is extracted from lateral zone, the efficiency decrease with the extraction temperature and increases with equivalence ratio. The highest efficiency reaches $\sim 96\%$ at $T_e = 500$ K and $\phi = 1$. The lowest efficiency of $\sim 41\%$ occurs at $T_e = 1100$ K and $\phi = 0.3$. Optimization on the burner’s geometry is performed to increase the heat extraction efficiency for heat extraction from lateral zones. A detailed GRI 3.0 mechanism is adopted to quantitatively predict the pollutant emissions. The temperature profiles obtained with GRI 3.0 mechanism vary with the ones obtained from single-step mechanism. Two major pollutants, NOx and CO, are simulated. The emission shows a positive correlation to the equivalence ratio and the flame temperature. Both pollutants have a high concentration at higher equivalence ratios and low extraction temperatures.
High Efficiency High Temperature Heat Extraction from Porous Media Reciprocal Flow Burner

by
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A thesis submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Master of Science in Mechanical Engineering

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DEDICATION

To my parents.
BIOGRAPHY

The author was born in Nanchong, Sichuan, China, a small town with great food and long history. He went to high school in Chongqing, a mountainous city famous for its hot weather and beautiful girls. After that he earned a bachelor's degree in mechanical engineering in Shanghai Jiao Tong University and now he's studying in North Carolina State University.

Outside school, Zhaoxi was an activist pushing for the publicity of government information in China. He also enjoys biking and swimming.
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**Greek symbols**

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**Subscripts**

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The development of small-scale and portable energy generators based on thermoelectric devices and Stirling engines requires high temperature sources capable to operate with high energy efficiency. Hydrocarbon fuels have high energy densities and remain preferable primary energy sources to supply high temperature loads. However, the low high temperature efficiencies of conventional burners and the urge to decrease pollutants released by combustion motivate the development of more effective burner designs. One of the promising designs is reciprocal flow burner (RFB). Compared to conventional burner, RFB
allows gaseous fuel to burn in a wide range of equivalence ratios, has a higher efficiency in terms of energy extraction, and generates lower NO$_x$ and CO emissions.

1.1 General Description

Gas phase combustion in porous media, or filtrational gas combustion, as Babkin [1] summarized, have been classified into different regimes according to propagation velocities of flames: low-velocity regime, high-velocity regime, sound velocity regime, low velocity detonation and normal detonation. The combustion process in RFB normally falls in to low-velocity regime. The flame can propagate either upstream or downstream, depending on the reaction rate and the flow speed. Kennedy et al. [2] reported that downstream propagation occurs when equivalence ratio $\phi \leq 0.45$ or $\phi \geq 1.7$ and upstream propagation occurs when $0.45 < \phi < 1.7$.

Porous media burners takes advantage of the strong interaction between solid and gas phases. The solid matrix absorbs and stores the energy released from combustion and transfers it to low temperature fuel/air mixture for preheating and ignition. The solid matrix generally has a high heat capacity, allowing it to keep a high temperature, thus sustaining the flame, resulting in a much wider range of flammable limit than combustion in free space. The heat recirculation process is shown in Fig. 1.1. In the solid matrix, due to its small conductive area (in the case of packed-bed, only point contact between pellets), the role of thermal conduction is limited, which leads to a steep temperate gradient to exist between flame and heat extractor. On the other hand, the high temperature and the large area of the porous media make radiation heat transfer between solid phase to play an important role [3].
Reciprocal flow burner, as its name suggests, changes flow direction periodically. Unlike conventional burner, RFB stabilizes a gaseous flame in a porous media using a self-adjusted heat recuperation process. In RFB, the combustion temperature of air/fuel mixture is independent of the adiabatic combustion temperature. The former could be lower (underadiabatic) or higher (superadiabatic) than latter. Superadiabatic or excess enthalpy combustion, which occurs when the flame propagates downstream, can have much higher temperature than adiabatic combustion. Hanamura et al. [5] showed a 13 times increase in flame temperature for extremely lean fuel/air mixture. Underadiabatic combustion occurs when the flame propagates upstream, where too much heat is extracted directly from the flame, resulting in a lower flame temperature.

### 1.2 Modeling of Porous Media Combustion

Due to the complexity and randomness of the porous media, a simulation of detailed chemical reaction and fluid dynamics in the interstice of matrix is both pointless and time-consuming. Therefore, a continuum assumption is usually applied [6]. Both solid and fluid phase are taken as continuum, overlapping on the same space. The advantage of this is
obvious. A macroscopic view is enough for simulation and the exact configuration of the solid-fluid interface is not required. By assuming continuum, the governing differential equations for flow in free space can be easily modified and applied. Even with simplification, three-dimensional models are rarely adopted, considering their heavy computational duties. Therefore, a one or two dimensional continuum model is normally adopted for simulation.

Uniform or locally uniform in porosity is common for various porous media. However, it is worth mentioning special cases that are focused on boundary conditions, where the uniformity near the impermeable wall is not applicable, especially for the point-contact packed-bed of pellets.[7]

A number of numerical models, one or two dimensional, have been developed to study the behavior of RFB. Contarin et al.[8], on whose work this thesis is heavily based, built a one-dimensional numerical model to study the efficiency of low temperature heat extraction using Fortran. In his configuration, the whole inner cavity of combustion chamber was filled with alumina pellets and two heat extractors were placed on both ends. He predicted the temperature profile and thermal energy output for equivalence ratios ranging from 0.15 to 0.65, filtration velocity of 20 cm/s and 30 cm/s. He showed that during a half cycle, the total power output had little variation as the flame propagated.

Bubnovich et al. [9] proposed a different approach. Unlike Contarin et al.’s solution, in which one set of differential equation governing the whole system, Bubnovich et al. divided the reactor into three regions: the pre-heating region, the moving reaction region, the post-combustion region, and derived governing equations separately for each one of them. In doing so, the three region can be solved analytically. His approach showed a satisfactory agreement with numerical model. Laguerre et al. [10] compared two simulated temperature
profiles, which were generated by commercial software Fluent and self-developed codes, respectively and they gave similar results. Zheng et al. [11] used a two-dimensional Fluent model to study inclinational instability of flame.

1.3 Parametric Studies

The performance of porous media burner is influenced mainly by three aspects, the design of reactor, the efficiency of heat extraction and the properties of air/fuel mixture. There are different burners adopting similar physical principle: reciprocal flow burner, counter flow burner (Fig. 1.2), double spiral burner (Fig. 1.3), etc. Even with the same burner type, the geometry and material of porous media can cause a big difference.

![Fig. 1.2 Counter flow burner by Belmont et al. [12]](image)

Gao et al. [14–16] conducted an extensive experimental research on the affect of solid matrix on double-layer burner, shown in Fig. 1.4. The upstream layer was composed of 3-mm alumina pellets. The downstream layer was set as the variable. Different porous media materials were tested: packed bed with 6, 8, 10, 13mm diameter alumina pellets,
200 cpsi (channel per square inch) alumina honeycombs and Cellular foam of different materials: alumina (Al₂O₃), zirconia (ZrO₂), iron-chromium-aluminum (FeCrAl) and silicon carbide (SiC). Nine thermocouples were placed symmetrically along the flow direction and a gas analyzer was used to measure the concentration of pollutants in the exhaust gas. These papers report the influence of solid matrix on flame temperature and on NOₓ and CO emissions.

Similar studies were conducted experimentally by Xie et al. [17] and Yu et al. [18]. Xie et al. examined various porous media (ceramic foam and alumina pellets with different diameters) in RFB and Yu et al. studied metal fiber, ceramic and stainless fin in flat burner.

Liu et al. [19] investigated the effect that the thermal conductivity of the wall has on the flame. In a lot of cases, the conductive heat transfer in the wall along the flow direction (axial direction) is neglected. The wall is assumed to be perfectly insulated, or only the heat transfer in the normal direction to the wall (radial direction) is taken into consideration. The work of Liu et al. shows that the conduction in the axial direction has a noticeable
effect for a meso-scale channel filled with high porosity fibrous porous medium. The paper considered the wall as a separate layer in a two dimensional simulation, the energy transferred upstream was enhanced by the wall. The larger thermal conductivity allowed a wider range of flammability limits, at the cost of thermal efficiency and required higher flow velocity.

While previous studies focus on a fully developed combustion, Wang et al. [20] studied experimentally the temperature changes in the developing stages. The temperatures during the startup and the switch-off stage in a packed-bed porous media were measured systematically. The relations between temperature and pellet diameter, air flow rate and equivalence ratio were recorded and analyzed.
A number of studies were devoted specifically to reciprocal flow burner rather than porous media combustion in general. For example, Hoffmann et al. [21] came up with a RFB design filled with three separated porous media regions with gap between them. High thermal conductivity of the porous media helps the performance in thermoelectric applications. But it reduced the porous media's ability to ‘lock-in’ energy. The direct energy extraction from the combustion zone was enhanced, increasing the instability of the flame. By setting three separated porous media zones, the flame is contained in the middle zone and the other porous media zone on both ends serves to enhance thermoelectric energy conversion. An analytical model was built. It predicted the heating value required to sustain the combustion and the location of the flame for different conductivities of porous media.

Another rather thorough research was conducted experimentally by Hoffmann et al. [22]. He discussed the influence of both solid phase properties (material, porosity) and gas phase properties (velocity, equivalence ratio and half cycle) on flammability limits and emissions. A surge in CO emission was predicted when the flow switched direction. The increase in CO emission was caused by incomplete combustion of hydrocarbons when the burning gas mixture went back to a cooler region. A temporary cut in fuel supply before the direction switching is suggested so that during the switching there would only be air in the combustion chamber.

The performance of packed bed reactors depends on material and structure of the porous medium [17, 21, 23], the geometry and properties of combustion chamber and the presence of catalyst [24]. The heat extraction can be performed with an intermediate heat exchanger [25] or directly with a thermoelectric energy converter [26].
1.4 Applications

Porous media combustion has a variety of applications other than a portable power source for small electronic devices, it can drive micro-turbines [27], or be used to generate synthesis gas [28]. The application with the most practical and commercial potentials is to power small portable electric devices. A thermoelectric device based on the Seebeck effect is normally combined with porous media burner to achieve the power conversion. When two chosen thermoelectric materials are subjected to different temperatures, the temperature difference can generate an electric potential. For fuel-lean mixtures, the flame temperature in porous media can be increased more than 10 times, providing the thermoelectric material the temperature difference it needs. Although the thermoelectric power conversion only has a limited efficiency, the energy recuperation in porous media burner can still make the product competitive. Compared to transitional battery, the energy density of hydrocarbon is more than two order of magnitude larger, which means, a hydrocarbon fueled thermoelectric system with 1% overall efficiency can output more electricity than its counterpart in traditional battery [29]. Besides, unlike traditional battery, the recharge for hydrocarbon based device is instant.

In one of his early works, Weinberg et al. [30] studied analytically an ideal thermoelectric device operating between temperature inside the combustion chamber and ambient temperature, shown in Fig. 1.5. Under an adiabatic condition, with an preheated incoming flow of extreme lean fuel-air mixture, in which the air content higher than 98.4%, the device had an overall efficiency of 0.197. A modification on the converter was made later by Weinberg himself, which brought the efficiency to a higher value of 0.218 [31].

Hanamura et al. [32] numerically studied another case of extremely lean gas in a RFB
Thermoelectric device by Weinberg et al. [30] with an equivalence ratio around 0.017 numerically. Unlike previous case, in which the porous media was inert, the porous media in this case also served as a catalyst, which led to a lower activation energy in the simulation. Dimensionless analysis was adopted in the paper and the relations between thermal efficiency and Peclet number, heating value and half cycle were presented. The efficiency of heat extraction reached an impressive 94%. The overall efficiency of 4.7% was limited by the thermoelectric conversion.

A number of closely-related studies were conducted by Karim et al. and Donoso-Garcia et al. Karim et al. [33] studied experimentally the catalyst characterization as well as the affect of flow velocity and equivalence ratio on temperature during both start-up and steady state. Donoso-Garcia et al. [34] built an FLUENT model for an inert porous media burner.
to evaluate the electric output and efficiency and pollutants emission under different equivalence ratios and flow velocities.

1.5 Thesis Objectives

In a number of applications, high temperature heat extraction is required for efficient operation. In this thesis, the efficiency of high temperature heat extraction from a RFB is studied numerically to analyze and optimize the heat extraction strategies. A time-average model is developed to predict the efficiency of high temperature heat extraction from a RFB and to perform parametric studies of heat extraction at various temperatures for lean and ultralean air/fuel mixtures. A detailed combustion mechanism is adopted to predict the NOx and CO production and to study the routes of pollutant emission. Further analysis is performed to study the influence of equivalence ratio and extraction temperature on pollutant emissions.
2.1 Geometry of the RFB

The RFB in this study (Fig. 2.1) has a reactor length $L = 0.8$ m and a packed bed with porosity $\epsilon = 0.4$ consisting of spherical alumina pellets with diameter of $d = 5.6$ mm. The burner is thermally insulated except for the two ends where heat loss bring the flow
temperature to an ambient temperature of 300K. The high temperature heat extractors are placed at central and lateral extraction zones with a length $L_e = 0.1$ m for each zone. Two heat loss zones are set at both ends of the reactor to constrain the flame with the same length $L_0 = 0.1$.

![Reciprocal flow burner](image)

**Fig. 2.1** Reciprocal flow burner (a) first half-cycle (b) second half-cycle.

The direction of air/fuel mixture is switched periodically and the energy equations for
solid and gas phases are represented as

\[
(1 - \epsilon) c_s \rho_s \frac{\partial T_s}{\partial t} = (1 - \epsilon) \frac{\partial}{\partial x} \left( [k_{s, eff} + k_{rad}] \frac{\partial T_s}{\partial x} \right) + h_v (T_g - T_s) - \beta_e (T_s - T_e) - \beta_0 (T_s - T_0) \tag{2.1}
\]

\[
\epsilon c_g \rho_g \frac{\partial T_g}{\partial t} = \epsilon \frac{\partial}{\partial x} \left( k_g \frac{\partial T_g}{\partial x} \right) - \epsilon c_g \rho_g v_g \frac{\partial T_g}{\partial x} + h_v (T_s - T_g) + H_{chem} W \tag{2.2}
\]

In the energy conservation equation for solid phase, the left hand side is the time differential of the thermal energy in the control volume. The first term in the right hand side is the conduction term. In the packed-bed, the pellets only have point contact between each other. Therefore an effective thermal conductivity needs to be estimated. Besides, the radiation inside the porous media has a strong contribution to the heat transfer in solid phase. Its influence is taken into consideration as part of the conduction term. The second term on the right hand side is the convection heat transfer between fluid and solid phase. The third term on the right hand side is the heat exchange between the reactor and the thermoelectric energy converter at a high extraction temperature \(T_e\) and the fourth term is the heat exchange at the end of the reactor, where the exhaust gas is cooled to ambient temperature. \(\beta_e\) and \(\beta_0\), the volumetric heat transfer coefficients, are functions of location. They have a positive value in the heat extraction zones and heat loss zones respectively and have a value of zero anywhere else.

In the energy conservation equation for fluid phase, similarly, the left hand side is the time differential of the thermal energy in the control volume. The first term in the right hand side is the conduction term and the second is the energy difference caused by the flow in and out the control volume. The radiation of the fluid phase is neglected. The third
term is the convection heat transfer between fluid and solid phase. The last term is the energy released by the reaction, where $H_{chem}$ is the heat of chemical reaction and $W$ is the reaction rate.

The species transport is represented as

$$\frac{\partial}{\partial t} (\rho y_i) = -\frac{\partial}{\partial x} (\rho v y_i) + \frac{\partial}{\partial x} (\rho D_{m,i} \frac{\partial y_i}{\partial x} + D_{T,i} \frac{\partial T}{\partial x}) + W_i \quad (2.3)$$

In the species transport equation, the left hand side is the time differential of the mass fraction of species $i$ in the control volume. The first term on the right hand side represents the mass fraction change caused by the flow in and out the control volume. The second term on the right hand side is the diffusion term, including mass diffusion and thermal diffusion, where $D_{m,i}$ and $D_{T,i}$ are the mass diffusion coefficient and thermal diffusion coefficient for species $i$ respectively.

### 2.2 Time-averaged Model

An one dimensional time-averaged model describing the burner performance is developed in FLUENT as shown in Fig. 2.2. This model is aiming to take a time average of the heat transfer process while the reacting flow going opposite directions. The model consists of two channels, sharing a highly conductive wall. As a result of the high conductivity, the local temperature equilibrium between the two channels can be achieved for all axial locations, which means the two channels will have the same temperature profile. In the two channels, the gas mixtures flow in opposite directions with a filtration velocity $v_g = 0.3$ m/s. This model is equivalent to a RFB with infinitesimal half-cycle. Although the half cycle has some
influence on temperature profile [22], its impact on power output is negligible [8]. The gas flow and heat transfer are assumed to only vary in axial direction. The porous media is considered to be homogeneous and the effective thermal conductivity of the packed bed is estimated as $k_{s,eff} = 0.005k_s$. The porosity change near the wall is neglected. The time-averaged model closely resembles a counter-flow reactor with infinitely conductive wall. Counter flow reactors have similar applications as RFB and were previously studied for fuel reforming and lean combustion [12, 35–37].

![Fig. 2.2 Time-averaged model in FLUENT represents the flow reversal as two flows in opposite directions separated by a highly conducted wall](image)

All heat extraction zones and heat loss zones are assumed to have the same volumetric heat exchange coefficient $\beta_0 = \beta_e = 5 \times 10^4 \text{W/m}^3 \cdot \text{K}$. This coefficient is chosen to be the same order of magnitude as in Contarin et al. [8] and large enough so that the temperature of the gas reaches balance with the temperature at which the heat is extracted for the whole temperature range. The reactor is preheated to $T_i = 1300 \text{ K}$. Although for RFB, the periodical changing of flow direction leads to a constantly self-adjusting combustion and heat recuperation process, the time-averaged model can reach a steady state. Local equilibrium of fluid and solid phase temperature is assumed considering the intense interaction
between them. The influence of the solid phase radiation is taken into consideration by adopting a radiative heat transfer coefficient $k_{rad} = 4F d \sigma T^3$ while the gas phase radiation is neglected.

Applying these assumptions, the governing equations can be simplified as

$$\frac{\partial}{\partial x} \left( k_{eff} \frac{\partial T}{\partial x} \right) = \beta_0 (T - T_0) + \beta_v (T - T_v) - \frac{1}{2} H_{chem} (W_1 + W_2)$$

(2.4)

where $k_{eff} = (1 - \varepsilon)(k_{s,eff} + k_{rad}) + \varepsilon k_g$.

$W_1$ and $W_2$ represents the reaction rate of the fuel, methane, in the upper and lower channels respectively. $W$ is described by one-step chemical reaction mechanism [38]

$$W = A e^{\left(-\frac{E_a}{RT}\right)} C_{CH_4}^a C_{O_2}^b$$

(2.5)

where $A = 2.119 \times 10^{11}$, $E_a = 2.207 \times 10^8$, $a = 0.2$, $b = 1.3$.

The species in the one channel do not interact with species from the other channel, because of the impermeable wall. Therefore the governing equations for species transport should be written separately for the two channels. The time differential term can be dropped under the steady state condition. The species transport equations for the upper and lower channels are represented as,

$$-\frac{\partial}{\partial x} (\rho v y_i) + \frac{\partial}{\partial x} (\rho D_{i,m} \frac{\partial y_i}{\partial x} + \frac{D_{T,i} \partial T}{T \partial x}) + W_i = 0$$

(2.6)

$$\frac{\partial}{\partial x} (\rho v y_i) + \frac{\partial}{\partial x} (\rho D_{i,m} \frac{\partial y_i}{\partial x} + \frac{D_{T,i} \partial T}{T \partial x}) + W_i = 0$$

(2.7)
Boundary conditions are imposed as:

\[ \begin{align*}
T(0) &= T(L) = T_0; & y_{p,1}(0) &= y_{p,2}(L) = 0; & \frac{\partial T}{\partial x}(0) &= \frac{\partial T}{\partial x}(L) = 0; & \frac{\partial y_{i,2}}{\partial x}(L) &= \frac{\partial y_{i,1}}{\partial x}(L) = 0 \\
\end{align*} \]  \tag{2.8}

The steady state simulation is much faster in FLUENT than a transient model, which allows a comprehensive parametric study. Several sets of simulations were run varying equivalence ratio \( \phi \), heat extraction temperature \( T_e \) and the extraction location. The time-averaged model is validated against experimental data of Contarin et al. [8], as shown in Fig. 2.3.

![Fig. 2.3 Numerically predicted temperature profiles validated against experimental data of Contarin et al. [8]. The solid line and the dashed line represent the Fluent result for equivalence ratio \( \phi = 0.25 \) and \( \phi = 0.58 \), respectively. The dots and hollow symbols represent experimental data for equivalence ratio \( \phi = 0.25 \) and \( \phi = 0.58 \), respectively.](image)
3.1 Heat Extraction from Central Zone

In the first case studied the heat is extracted from the central zone of the reactors. The steady state temperature profile for an equivalence ratio of $\phi = 0.3$ and extraction temperature $T_e = 500K$ is shown in Fig. 3.1. The large value selected for $\beta_e$ leads to a drastic drop in temperature at the central zone to reach the heat extraction temperature $T_e$ and gives a symmetric M-shaped temperature profile. The peaks of the profile on both sides
of the central zone correspond to the combustion zones. In a RFB, when the gas mixture flow from left to right in the first half-cycle, the thermal energy is transmitted from solid phase to gas phase in positive temperature gradient zone near the inlet till the temperature reaches the gas ignition point. The thermal energy is stored back in solid phase from gas phase in the negative temperature gradient zone near the outlet to heat the incoming gas mixture in the following half-cycle when flow switches direction. This process will cause an asymmetry in temperature profile. The peak temperature on the upstream will move further away from the inlet. In the time-averaged model, the energy transmission in the two half-cycles happens simultaneously. On the left end of the model, the thermal energy is transferred from the burnt gas in lower channel to the unburned gas in the upper channel. The energy is transferred in the opposite direction in the right end of the model.

Fig. 3.1 Temperature profile for heat extraction from the central zone at $\phi = 0.3$, $T_e = 500$ K.
The heat extraction efficiency $\eta$ is defined as the ratio of heat extraction rate to the chemical energy of the flow based on lower heating value:

$$\eta = \frac{\dot{Q}_e}{\dot{m} H_{chem}} = \frac{\dot{Q}_e}{\dot{m} \gamma LHV}$$

(3.1)

To find out the influence of extracting temperature and equivalence ratio, a series of simulations is conducted with $T_e$ ranging from 500 K to 1100 K with an increment of $\Delta T_e = 100$ K and $\phi$ ranging from 0.3 to 1.0. As shown in Fig. 3.2, the efficiency of the heat extraction from the central zone is very low. In all the cases studied, the efficiency is less than 6%. The efficiency decreases as the extraction temperature increases in a seemly second-order relation, with a steeper slope for lower extraction temperature. As for the influence of equivalence ratio, the efficiency decreases with the equivalence ratio increase in a nonlinear pattern. A larger difference in efficiencies is shown at low equivalence ratios. As the equivalence ratio increases, the efficiency appears to reach a lower bound, determined by the burner’s properties such as material and geometry.
3.2 Heat Extraction from Lateral Zones

In the second case the heat is extracted from the lateral zones of the channels, The steady state temperature profile for an equivalence ratio $\phi = 0.3$ and extraction temperature $T = 500\text{K}$ is shown in Fig. 3.3. In the middle section between the two lateral heat extraction zones, there is no heat extraction nor heat loss, therefore the temperature profile appears as a flat line. Compared with Fig. 3.1, the maximum temperature remains the same.

As shown in Fig. 3.4 with a solid line, the efficiency is much higher than the one in...
previous case, especially on low temperature end where the efficiency reaches 90%. The efficiency shows a slightly non-linear relationship with extracting temperature with steeper slopes for lower equivalence ratios, and a non-linear relationship with equivalence ratio with a larger difference at the low equivalence ratio end. Though in this case, efficiency decreases as the equivalence ratio increases. The limit in efficiency, which serves as an upper bound in this case, still exists as the equivalence ratio approaches 1.0.
3.3 Heat Extraction from Central and Lateral Zones

In the third case the heat is extracted from the central and lateral zones of the channels simultaneously. The steady state temperature profile for an equivalence ratio $\phi = 0.3$ extraction temperature $T = 500\text{K}$ is shown in Fig. 3.5. Compared with Fig. 3.3, the peak temperature remains constant.

As shown in Fig. 3.4 with a dashed line, the efficiencies in this and previous cases are very similar. Only a limited increase at low equivalence ratios and high temperatures is
observed. Naturally, they share the same relationship with extracting temperature and equivalence ratio. The increase in efficiency at high equivalence ratio is barely noticeable, which means adding an extra extraction zone in the center only redistributes the heat extraction between extractors rather than increases it.

### 3.4 Optimization

Although the efficiency of heat extraction from lateral zone at lower temperature reaches as high as 90%, the efficiency at higher temperatures still has a lot of room for improvement. As stated in previous section, adding heat extraction zone in the center has almost no influence on efficiency. So another approach is adopted. A modification of geometry is
made based on analysis of Eq. (2.4). Integral of both sides of Eq. (2.4) for interval $[0, a]$ gives:

$$k_{eff} \frac{\partial T_g}{\partial x} \bigg|_a = \int_0^a \beta_0 (T_s - T_0) \, dx + \int_0^a \beta_e (T_s - T_e) \, dx + \frac{1}{2} \int_0^a H_{chem} (W_1 + W_2) \, dx \quad (3.2)$$

If interval $[0, a]$ only covers heat loss zone, where there is no reaction and no heat extraction, then

$$k_{eff} \frac{\partial T_g}{\partial x} \bigg|_a = \int_0^a \beta_0 (T_s - T_0) \, dx \quad (3.3)$$

As a result, the efficiency of the heat extraction can be expressed as

$$\eta = 1 - 2 \int_0^a \frac{\beta_0 (T_s - T_0) \, dx}{\dot{m} H_{chem}} = 1 - 2 \frac{k_{eff} \frac{\partial T_g}{\partial x} \bigg|_a}{\dot{m} H_{chem}} \quad (3.4)$$

The efficiency is controlled by the temperature gradient and the effective thermal conductivity. Therefore, a geometry change to reduce the temperature gradient near the heat loss zone can increase the efficiency. To prove this hypothesis, additional sections of porous material were added between the lateral heat-extraction zones and heat-loss zones to extend lateral packed beds, shown in Fig. 3.6.

As shown in Fig. 3.7, the temperature profile shows a flatter slope between the lateral heat-extraction zones and heat-loss zones, which indicate a thorough heat exchange between the low temperature unburnt gas and the high temperature exhaust gas. More energy is brought back to the system rather than lost through heat loss zone. The efficiency increases impressively, lifting the upper bound towards one in the whole temperature range, as shown in Fig. 3.8. The efficiency reaches around 95% even at the high temperature end.
Fig. 3.6 The original geometry of RFB (top) and the optimized geometry of the RFB (bottom).

Fig. 3.7 Temperature profile for optimized heat extraction from the lateral zones at $\phi = 0.3$, $T_e = 500$ K.
Fig. 3.8 Optimized efficiency of heat extraction from the lateral zone, where the dashed lines and solid lines represent the efficiency of heat extraction from the lateral zones with and without optimization, respectively.

The one dimensional time-averaged model gives basic description and understanding of the high temperature heat extraction from RFB. There are several aspects that can be further studied for more accurate and realistic results. A multi-step chemical mechanism can be adopted instead of the one-step mechanism used in this study. The turbulence in flow and the heat loss from boundaries can be taken into consideration. Finally porous media with different materials and structures can be studied.
4.1 Motivation

The one-step mechanism adopted in previous section gives fast and comprehensive results in terms of thermal energy transfer in the RFB. But it provides little information on the flame chemistry. One of the advantages possessed by RFB is that at high equivalence
ratios, the under-adiabatic combustion generates low temperature flames, with low NOx and CO emission. NOx normally refers to two pollutants, NO and NO2, both poisonous. Like CO2, NOx emission occurs in nature as well, mostly from decomposition of organics in soil and ocean. The emission from human activities is mainly from fossil fuel combustion, both moving sources like cars and airplanes and stationary sources like power plants. NOx has serious damaging affect on the environment. It can cause acid rain. Under the exposure to ultraviolet light, NOx forms photochemical smog, which can harm both human immune system and vegetation.

CO is a known deadly gas, mostly produced by incomplete combustion of hydrocarbon and coal. It can cut down oxygen transportation in human blood cells and lead to suffocation.

Considering the harm these pollutants can cause, it is important to determine quantitatively how much emission was produced. Adopting a more detailed chemical mechanism can quantitatively determine the amount of emission. To achieve this, a detailed GRI 3.0 mechanism in Chemkin format is introduced into FLUENT. GRI mechanism is a mechanism designed to model natural gas combustion. It is funded by Gas Research Institute and released by UC-Berkly [39]. The newest 3.0 version contains 53 species and 325 elementary reactions, including NOx formation and re-burning.

4.2 Comparison between Mechanisms

First we wish to check the validity of the single-step mechanism used in previous sections. GRI 3.0 mechanism is employed in four cases: $\phi = 0.3$ and $T_e = 500$ K, $\phi = 0.3$ and $T_e = 1100$ K, $\phi = 0.9$ and $T_e = 500$ K, $\phi = 0.9$ and $T_e = 1100$ K. The simulated temperature
profiles are plotted against single-step mechanism with the same conditions, as shown in Fig. 4.1-4.4.

As shown in these figures, with $\phi = 0.3$, the thermal wave front moves slightly downstream with GRI 3.0 and the maximum temperature drops to varying degrees. With $\phi = 0.9$, the thermal wave front moves slightly upstream. For the first three cases, the differences between temperature profiles are very small, which means the single-step mechanism gives a satisfactory prediction. However in the last case, where the equivalence ratio $\phi = 0.9$, $T_e = 1100$ K, there is a rather large temperature drop ($\sim 200$ K) in the combustion zone. Fig. 4.4 shows that the flame is located near the boundary of the heat extraction region.

**Fig. 4.1** Temperature profiles for heat extraction from the lateral zone at $\phi = 0.3$, $T_e = 500$ K obtained with single-step mechanism (solid line) and the GRI 3.0 mechanism (dashed line).
Fig. 4.2 Temperature profile for heat extraction from the lateral zone at $\phi = 0.3$, $T_e = 1100$ K obtained with single-step mechanism (solid line) and the GRI 3.0 mechanism (dashed line).

and the insulated region, which indicates that a slight shift of the flame position can have a huge influence on how much energy is directly drained from the flame. In this case, a shift towards upstream direction put the flame inside the heat extraction zone, making it a typical case of underadiabatic combustion. But even with this temperature drop, the heat extraction efficiency is not heavily affected, 77.0% compared with 77.9% for the single-step mechanism.
Fig. 4.3 Temperature profile for heat extraction from the lateral zone at $\phi = 0.9$, $T_e = 500$ K obtained with single-step mechanism (solid line) and the GRI 3.0 mechanism (dashed line).
Fig. 4.4 Temperature profile for heat extraction from the lateral zone at $\phi = 0.9$, $T_e = 1100$ K obtained with single-step mechanism (solid line) and the GRI 3.0 mechanism (dashed line).
4.3 Mechanisms of NO\textsubscript{x} Formation

Miller and Bowman [40] gave a detailed review on NO formation in combustion. They presented three major mechanism, thermal (Zeldovich) NO mechanism, prompt (Fenimore) NO mechanism and N\textsubscript{2}O-intermediate mechanism. Later a new route for NO formation was discovered as NNH route [41]. All of the four mechanisms are illustrated in the following sections.

4.3.1 Thermal NO

The thermal NO\textsubscript{x} mechanism has three principle reaction

\begin{align*}
N_2 + O &\rightleftharpoons NO + N \\
N + O_2 &\rightleftharpoons NO + O \\
N + OH &\rightleftharpoons NO + H
\end{align*}

The mechanism is also known as Zeldovich mechanism or extended Zeldovich mechanism, for the first two reactions first recognized by Zeldovich. The reactions require high temperature (1700 K) to have a fast generation. So although this mechanism contains major radicals like OH, in many algorithms, for example the built-in thermal NOx calculation in Fluent, it is calculated separately from the combustion and viewed as post-processing. Thermal NO can be produced where the burner is unevenly heated and high temperature spots occur. In porous media combustion, the solid matrix and the active interaction between two phases help to dissipate energy and to eliminate high temperature spots.
4.3.2 Prompt NO

Prompt NO formation was first identified by Fenimore. It occurs at a lower temperature compared to thermal NO, and is heavily influenced by the concentration of hydrocarbon fuel. It's normally produced close to the flame and it is an important component to the total NO production in low temperature combustion. The prompt NO mechanism includes 6 elementary reactions,

\[ \text{CH} + \text{N}_2 \rightleftharpoons \text{HCN} + \text{N} \quad (4.4) \]
\[ \text{C} + \text{N}_2 \rightleftharpoons \text{CN} + \text{N} \quad (4.5) \]
\[ \text{HCN} + \text{O} \rightleftharpoons \text{NCO} + \text{H} \quad (4.6) \]
\[ \text{NCO} + \text{H} \rightleftharpoons \text{NH} + \text{CO} \quad (4.7) \]
\[ \text{NH} + \text{H} \rightleftharpoons \text{N} + \text{H}_2 \quad (4.8) \]
\[ \text{N} + \text{OH} \rightleftharpoons \text{NO} + \text{H} \quad (4.9) \]

4.3.3 \text{N}_2\text{O}-Intermediate NO

\text{N}_2\text{O} is famously known as the laughing gas and itself is a major greenhouse gas. It is also used in racing or military vehicle as a combustion agent to achieve a sudden burst of speed. In this mechanism, \text{N}_2\text{O} is produced in large amount in the the flame region, and rapidly transform to NO. The \text{N}_2\text{O}-intermediate reaction mechanism can be represented by the following equations.

\[ \text{N}_2\text{O} + \text{O} \rightleftharpoons \text{N}_2 + \text{O}_2 \quad (4.10) \]
\[ \text{N}_2\text{O} + \text{O} \rightleftharpoons 2\text{NO} \quad (4.11) \]
\[ \text{N}_2\text{O} + \text{H} \rightleftharpoons \text{N}_2 + \text{OH} \quad (4.12) \]
\[ \text{N}_2\text{O} + \text{M} \rightleftharpoons \text{N}_2 + \text{O} + \text{M} \quad (4.13) \]
\[ \text{NH} + \text{NO} \rightleftharpoons \text{N}_2\text{O} + \text{H} \quad (4.14) \]
\[ \text{NCO} + \text{NO} \rightleftharpoons \text{N}_2\text{O} + \text{CO} \quad (4.15) \]

### 4.3.4 NNH Route NO

NNH route is a relatively new mechanism for NO formation. It proves to be important under certain conditions. Its process can be represented by the following three reactions.

\[ \text{NNH} \rightleftharpoons \text{N}_2 + \text{H} \quad (4.16) \]
\[ \text{NNH} + \text{M} \rightleftharpoons \text{N}_2 + \text{H} + \text{M} \quad (4.17) \]
\[ \text{NNH} + \text{O} \rightleftharpoons \text{NH} + \text{NO} \quad (4.18) \]

### 4.4 Results for NO Emission

#### 4.4.1 Influence of Equivalence Ratio

The equivalence ratio is naturally the first parameter that we want to discuss. The hydrocarbon fuel-to-air ratio does not only influence the flame temperature but also the concentration of radicals like H and OH.
Fig. 4.5 shows, unsurprisingly, the NO emission increases with the equivalence ratio. The fitted curve seems to suggest a second order relation between them, with the NO concentration increasing faster at high equivalence ratios. For the extraction temperature $T_e = 500$ K, the NO concentration in the exhaust gas increases smoothly from less than 1 ppm to 5 ppm when the equivalence ratio increases from 0.3 to 0.7, and sours to more than 15 ppm when equivalence ratio $\phi$ reaches 0.9. The emission with extraction temperature $T_e = 1100$ K shares the same trend and the emission levels coincide when $\phi$ is less than 0.4. For $\phi$ larger than 0.4, the difference between the two lines increases with $\phi$.

A common way to normalize emission is to calculate the emission per fuel consumption. In this study we choose to define the emission index of NO ($E_{\text{NO}}$) as the mass ratio of NO emission and fuel consumption.

$$E_{\text{NO}} = \frac{m_{\text{NO}}}{m_{\text{CH}_4}} \text{ (mg/kg)}$$ (4.19)

The emission index is plotted in Fig. 4.6. The two lines keep a similar trend as those in Fig. 4.5.
Fig. 4.5 NO emissions against equivalence ratio with extraction temperature of $T_e = 500$ K and $T_e = 1100$ K.
Fig. 4.6 Emission index of NO emission against equivalence ratio with extraction temperature of \( T_e = 500 \) K and \( T_e = 1100 \) K.
4.4.2 Influence of Extraction Temperature

As shown in previous section, the extraction temperature has little influence at the low equivalence ratios. So a high equivalence ratio $\phi = 0.9$ was chosen to be our focus. We can see from Fig. 4.7, the relation of extraction temperature and NO emission appears as a nice parabolic curve, with the maximum NO concentration located between $T_e = 600$ K and 700 K. As the emission is heavily influenced by flame temperature, a flame temperature against extraction temperature is plotted as Fig. 4.8. The flame temperature shows an identical trend as the emission, with the highest temperature located between $T_e = 600$ K and 700 K.

![Fig. 4.7 NO emission with equivalence ratio $\phi = 0.9$ against extraction temperature.](image)
Fig. 4.8 Peak flame temperature with equivalence ratio $\phi = 0.9$ against extraction temperature.
4.4.3 Routes of NO Formation

In this section, different routes of NO formation are respectively analyzed. Three cases were studied.

The first case, with $\phi = 0.3$, $T_e = 500$ K, shown in Fig. 4.9, has a total NO emission less than 1 ppm. The four mechanisms, thermal, prompt, N$_2$O-intermediate and NNH route, are all plotted accordingly. NNH route and N$_2$O-intermediate appear to be the most dominant route for NO formation. Surprisingly, the direct summation, represented by the symbol $\Sigma$, only reaches a little more than one half of the total emission. However, when all four mechanisms were taken into consideration simultaneously, the result is very close to the one from the full GRI 3.0 mechanism, except for at the right end of the burner, the result of GRI 3.0 mechanism shows that NO transferred to other species and the four mechanisms all fail to predict that.

The second case, with $\phi = 0.9$, $T_e = 500$ K, shown in Fig. 4.10, has a total NO emission around 22 ppm. The four mechanisms, thermal, prompt, N$_2$O-intermediate and NNH route, are all plotted accordingly. Prompt NO seems to be the major contribution to the total NO emission and N$_2$O-intermediate, one of the major NO formation route, is not significant in this case. Once again, the direct summation of the four mechanisms is smaller than the total emission by a large margin and when all four mechanisms were run together, the result shows a great agreement with full GRI 3.0 mechanism. The reduction of NO at the right end is still not predicted by the four mechanisms.

The third case, with $\phi = 0.9$, $T_e = 1100$ K, shown in Fig. 4.11, has a similar structure as the second case, only that the total emission drops to 11 ppm. The two stages of the NO at the right end of the GRI 3.0 curve, indicate that the mechanism responsible for the NO
Fig. 4.9 Routes of NO formation with equivalence ratio $\phi = 0.3$ and extraction temperature $T_e = 500$ K. The $\Sigma$ represents the numerical summation of the results for thermal mechanism, prompt mechanism, $N_2O$-intermediate route and NNH route. The thermal+prompt+$N_2O$-intermediate+NNH represents the results of the four mechanism calculated simultaneously. The results are shown for the upper channel, flow direction from left to right.

reduction, whatever it is, is temperature sensitive.

NNH route has a steady contribution in all three cases and the thermal mechanism remains unimportant in all three cases. Considering the maximum temperature this study encountered is just above 1700 K, it is understandable that the thermal mechanism, which only work at a meaningful speed at high temperatures, has little to contribute. Prompt mechanism gains more importance at higher equivalence ratios, regardless what temperature it is. $N_2O$-intermediate route, on the contrary, loses importance at high equivalence ratios.
Fig. 4.10 Routes of NO formation with equivalence ratio \( \phi = 0.9 \) and extraction temperature \( T_e = 500 \) K. The \( \Sigma \) represents the numerical summation of the results for thermal mechanism, prompt mechanism, \( N_2O \)-intermediate route and NNH route. The thermal+prompt+\( N_2O \)-intermediate+NNH represents the results of the four mechanism calculated simultaneously. The results are shown for the upper channel, flow direction from left to right.
Fig. 4.11 Routes of NO formation with equivalence ratio $\phi = 0.9$ and extraction temperature $T_e = 1100$ K. The $\Sigma$ represents the numerical summation of the results for thermal mechanism, prompt mechanism, $N_2O$-intermediate route and NNH route. The thermal+prompt+$N_2O$-intermediate+NNH represents the results of the four mechanism calculated simultaneously. The results are shown for the upper channel, flow direction from left to right.
4.5 **Mechanism for NO$_2$ Formation**

GRI 3.0 mechanism predicts a NO concentration drop near the outlet of the burner. According to our study, the missing NO is transferred into NO$_2$. The chemical process can be represented by the following reactions.

\[
\begin{align*}
\text{NO} + \text{HO}_2 & \rightleftharpoons \text{NO}_2 + \text{OH} \quad (4.20) \\
\text{NO} + \text{O} + \text{M} & \rightleftharpoons \text{NO}_2 + \text{M} \quad (4.21) \\
\text{NO}_2 + \text{O} & \rightleftharpoons \text{NO} + \text{O}_2 \quad (4.22) \\
\text{NO}_2 + \text{H} & \rightleftharpoons \text{NO} + \text{OH} \quad (4.23) \\
\text{NO}_2 + \text{CN} & \rightleftharpoons \text{NCO} + \text{NO} \quad (4.24)
\end{align*}
\]

4.6 **Results for NO$_2$ Emission**

In all three cases, the missing NO is transferred to NO$_2$, as shown in Figs. 4.12-4.14. The summation of profiles of NO and NO$_2$ flattened the drop at the right end of GRI 3.0's prediction. As all the nitrogen in NO still remains in the form of NOx, it is safe to say that the four mechanisms were good enough to predict NOx emission with a reasonable accuracy.
Fig. 4.12 Profiles for NO and NO$_2$ at equivalence ratio $\phi = 0.3$ and extraction temperature $T_e = 500$ K. The results are shown for the upper channel, flow direction from left to right.
Fig. 4.13 Profiles for NO and NO$_2$ at equivalence ratio $\phi = 0.9$ and extraction temperature $T_e = 500$ K. The results are shown for the upper channel, flow direction from left to right.
Fig. 4.14 Profiles for NO and NO$_2$ at equivalence ratio $\phi = 0.9$ and extraction temperature $T_e = 1100$ K. The results are shown for the upper channel, flow direction from left to right.
4.7 NO\textsubscript{x} Emissions

In this section we consider the total NO\textsubscript{x} emission. In Fig. 4.15, NO\textsubscript{2} and NO are comparable for extraction temperature $T_e = 500$ K. Both share the same trend as discussed before. But for $T_e = 1100$ K, NO\textsubscript{2} concentration is almost negligible (Fig. 4.16).

Similarly to the emission index of NO, the emission index for NO\textsubscript{x} is defined as the mass ratio of NO\textsubscript{x} emission and fuel consumption,

$$E_{I\text{NO}_x} = \frac{\dot{m}_{NO_x}}{\dot{m}_{CH_4}} \text{ (mg/kg)} \quad (4.25)$$

The $E_{I\text{NO}_x}$ is plotted against equivalence ratio (Fig. 4.17-4.18). Considering the fact that NO is very active in the air and will react with oxygen to form NO\textsubscript{2}, NO will cause the same impact on the environment as NO\textsubscript{2}. But the molecular weight of NO, 30, is different as NO\textsubscript{2}, 46. It is difficult to justify a direct summation of their mass. Therefore, an adjusted summation is defined by transferring the weight of NO\textsubscript{2} to the equivalent amount of NO,

$$\dot{m}_{adj\text{ NO}_x} = \dot{m}_{NO} + \frac{30}{46} \dot{m}_{NO_2} = \dot{m}_{NO} + 0.652 \dot{m}_{NO_2}. \quad (4.26)$$

Hence the corresponding emission index is defined as,

$$E_{I_{adj\text{ NO}_x}} = \frac{\dot{m}_{NO} + 0.652 \dot{m}_{NO_2}}{\dot{m}_{CH_4}} \text{ (mg/kg).} \quad (4.27)$$

The adjusted emission index is also plotted in Figs. 4.17-4.18.
Fig. 4.15 NOx emission against equivalence ratio with extraction temperature of $T_e = 500$ K. The results for NO, NO2 and the summation of them are plotted.
The results for NO, NO2 and the summation of the them are plotted.
Fig. 4.17 Emission index for NOx against equivalence ratio with extraction temperature of $T_e = 500$ K. The results for NO, NO2, the direct and adjusted summation of the them are plotted.
Fig. 4.18 Emission index for NOx against equivalence ratio with extraction temperature of $T_e = 1100$ K. The results for NO, NO2, the direct and adjusted summation of the them are plotted.
4.8 CO Emission

Carbon monoxide is an intermediate product of methane oxidation (Fig. 4.19).

Following the same procedure as in previous section, CO emission is plotted against equivalence ratio, as shown in Fig. 4.20. For high extraction temperature $T_e = 1100$ K, the equivalence ratio has a limited effect on CO emission. But with $T_e = 500$ K, the CO emission surges up.

The emission index of CO is defined as the mass ratio of CO emission and fuel consump-
Fig. 4.20 CO emission against equivalence ratio with extraction temperature of $T_e = 500$ K and $T_e = 1100$ K.

The emission index for CO is plotted in Fig. 4.21. It remains the same trend as in Fig. 4.20. For fuel-lean hydrocarbon fuel, the majority of CO is consumed by excessive air. The amount that remains is controlled by the temperature. Since at higher equivalence ratio, the extraction temperature seems to have the largest influence, we plot the CO concentration against the extraction temperature with $\phi = 0.9$. We can see the curve fit with the temperature curve in Fig. 4.8.
Fig. 4.21 Emission index for CO against equivalence ratio with extraction temperature of $T_e = 500$ K and $T_e = 1100$ K.
**Fig. 4.22** CO emission with equivalence ratio $\phi = 0.9$ as a function of extraction temperature.
A time-averaged model was developed to predict the behavior and efficiency of a RFB with heat extraction in different zones with different equivalence ratios at different temperatures. This model transferred a time-consuming transient state simulation into a faster steady state simulation. The results show that heat extraction from the central zone has a low efficiency. For extraction temperature from 500 K to 1100 K and equivalence ratio from 0.3 to 1.0, the maximum efficiency is lower than 6%. Heat extraction from lateral zones has a higher efficiency ranging from 40% to more than 90% under the same condition. Extraction
from both zones, though gives a different temperature profile, shows a very limited increase in efficiency compared to extraction from lateral zones. However, an optimization to control the heat flux towards heat loss zones by extending the packed bed largely improves the efficiency, especially at the higher temperature end, bringing the efficiency to more than 90% in the whole range of extraction temperatures and equivalence ratios.

A detailed GRI 3.0 mechanism is adopted to quantitatively predict the pollutant emissions. The temperature profiles obtained with GRI 3.0 mechanism vary with the ones obtained from single-step mechanism. With $\phi = 0.9$ and $T_e = 1100$ K, the simulated flame temperature drops around 200 K in GRI 3.0 mechanism. Two major pollutants, NOx and CO, are calculated. The emission shows a positive correlation to the equivalence ratio and the flame temperature. Not surprisingly, both pollutants has a higher concentration at higher equivalence ratio. What’s interesting is that with high extraction temperature, the emission level decreases. With the same equivalence ratio of 0.9, NOx emission increases from 12 ppm to 22 ppm when the extraction temperature decreases from 1100 K to 500 K. The effect is even more dramatic for CO. CO emission increases from 2 ppm to 30 ppm when the extraction temperature decreases from 1100 K to 500 K.
References


