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A Numerical Investigation of Natural Gas-Diesel Dual Fuel Engine Combustion and Emissions Using CFD Model

Yu Li

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A Numerical Investigation of Natural Gas-Diesel Dual Fuel Engine Combustion and Emissions Using CFD Model

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Dissertation submitted to the
Benjamin M. Statler College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Mechanical Engineering

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Morgantown, West Virginia
2018

Keywords: Dual fuel engine; Natural gas; NO₂ emission; CH₄ emission; CO emission;
Instantaneous kinetic study; CFD.

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Abstract

A Numerical Investigation of Natural Gas-Diesel Dual Fuel Engine Combustion and Emissions Using CFD Model

Yu Li

Natural gas (NG)-diesel dual fuel engines have been highlighted for their fuel flexibility and high thermal efficiency comparable to diesel engines. However, the addition of NG to compression ignition diesel engines was reported to elongate ignition delay and to increase the emissions of carbon monoxide (CO), unburned methane (CH₄), and nitrogen dioxide (NO₂). Past research on dual fuel engines has focused on the experimental research on the engine performance, combustion process, and exhaust emissions. The research on detailed mechanism dominating the impact of CH₄ on formation of CO and NO₂ in cylinder, and the mechanism for CH₄ to survive the combustion process and slip through the cylinder is limited. The examinations of these mechanisms require the simulation of dual fuel engine combustion using a CFD model coupled with chemical kinetic mechanism.

This research numerically investigates the combustion process and exhaust emissions from two NG-diesel dual fuel engines using a CFD model coupled with a reduced primary reference fuel (PRF) chemistry. The CFD model used is Converge-SAGE model with a maximum of 300000 grid points. The fuel chemistry used is a reduced PRF mechanism with 45 species and 142 reactions including a reduced NO_x mechanism with 4 species and 12 reactions. The CFD model with reduced PRF chemistry has been validated against experimental data measured in a single-cylinder compression-ignition engine over a wide range of CH₄ substitution ratio. A post-processing tool has been developed to calculate, analyze, and visualize the instantaneous rate of production (ROP) of key species in each cell with the known temperature, pressure, and species concentration exported by CFD code. The simulation results are further post-processed to numerically investigate the combustion process and the formation mechanism of CO, and NO₂ in a dual fuel engine. The mechanism for CH₄ to survive the main combustion process and post-combustion oxidation process is numerically examined.

The research on NO₂ formation identified $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ as the key reaction dominating the increased formation of NO₂ in dual fuel engines. The HO₂ necessary for the formation of NO₂ emitted by the engine is produced through the post-oxidation of CH₄ that survived the main combustion process. The CO emitted from the NG-diesel dual fuel engine is formed through the oxidation of CH₄ during the late

combustion process and post-combustion CH₄ oxidation. The CH₄ that survived the main combustion and post-combustion oxidation process is mainly distributed in region far from the spray plume of the pilot fuel and its combustion products.

This research also examined approaches capable of significantly reducing the emissions of CH₄ from a dual fuel engine. The preliminary results concluded that CH₄ emissions can be significantly reduced through optimizing injection timing, and the application of two-pulse fuel injection strategy. Adjusting injector fuel spray angle can also significantly reduce CH₄ emissions which should be considered in developing dedicated dual fuel engine.

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Nomenclature

0D Zero dimensional	ISDP Instantaneous species destruction pathway
ATDC After top dead center	IVC Intake valve close
BMEP Brake mean effective pressure	LES Large eddy simulation
CA Crank angle	LTC Low temperature combustion
CFD Computational fluid dynamics	NG Natural gas
CH ₄ Methane	NO Nitric oxide
CI Compression ignition	NO ₂ Nitrogen dioxide
CO Carbon monoxide	NO _x Oxides of nitrogen
DNS Direct numerical simulation	NRC National Research Council
EGR Exhaust gas recirculation	PCP Peak cylinder pressure
ER Equivalence ratio	PM Particular matter
EVO Exhaust valve open	PRF Primary reference fuel
GHG Greenhouse gas	QHCV Quasi-homogeneous constant volume
H ₂ Hydrogen	RCR Representative creation reaction
HC Hydrocarbon	RDR Representative destruction reaction
HCCI Homogeneous charge compression ignition	RNR Representative endothermic reaction
HD Heavy-duty	RXR Representative exothermic reaction
HRR Heat release rate	
HTC High temperature combustion	

ROP Rate of production

RRC Reaction rate constant

SI Spark ignition

TDC Top dead center

WSR Well stirred reactor

Chapter 1 Introduction

1.1 Background

Natural gas (NG) has been recognized as a viable clean alternative fuel for its abundant resource, attractive features of producing less greenhouse gas (GHG) benefiting from methane (CH_4), reduced emissions of pollutants, especially particulate matter (PM), and high thermal efficiency. NG can be burned as the sole fuel in spark ignition (SI) engines [1, 2] or as supplemental fuel in compression ignition (CI) diesel engines by dual fuel mode with NG added into the intake air [3, 4]. The NG-diesel dual fuel engine is well known for its low particulate matter (PM), oxides of nitrogen (NO_x) emissions as well as high thermal efficiency comparable to that of diesel engines. However, the addition of NG to a CI diesel engine was reported to extend the ignition delay, increase the emissions of carbon monoxide (CO), unburned CH_4 , and nitrogen dioxide (NO_2) [4]. Past research on dual fuel engines has focused on the experimental research on the engine performance, combustion process, and exhaust emissions. The detailed research on the factors dominating the impact of CH_4 on ignition delay, formation of CO and NO_2 in cylinder, and the mechanism for CH_4 to survive the combustion process and slip through the cylinder is limited. The examination of these mechanisms requires the simulation of dual fuel engines using a computational fluid dynamic (CFD) model coupled with a chemical kinetic model.

Numerical method has been recognized as a viable approach to better understand the combustion process in a NG-diesel engine. The combustion process and exhaust emissions from CI engine can be simulated using single zone, multizone, and CFD model. The single zone and multi-zones models developed in 1980s were able to accurately predict the heat release process, and to reasonably estimate the formation NO_x in CI diesel engines. The quasi-steady single zone model with detailed fuel chemistry has been widely applied to develop and validate the chemical reactions of the primary reference fuel (PRF) including n-heptane and iso-octane, and surrogate fuels measured using well-stirred reactors (WSR) [5], rapid compression machines [6], or shock-tubes [7, 8]. However, it is difficult to simulate the detailed combustion process and pollutants formation mechanism of modern diesel engines using the single-zone and multi-zone models due to the lack of detailed sub models accounting for the complex physical phenomena such as spray break, atomization, vaporization, species diffusion and transportation, and turbulence-chemistry interaction.

The current software for post-processing the simulation results exported by a CFD code mainly focus on the distribution of the key parameters such as temperature, equivalence ratio (ER), and key species. There is currently no convenient tool for researchers to examine the instantaneous rate of production (ROP) using commercial CFD models. This makes it difficult for researchers to solve fundamental chemistry problems using CFD. Therefore, the approaches and tools deriving the instantaneous

ROP data and its further analysis in a CFD model is essential.

1.2 Objective of this research

The objective of this research is to numerically investigate the combustion process and pollutant formation chemistry in NG-diesel dual fuel engine using CFD models, examine the formation mechanisms of CO, and NO₂ in the cylinder, and the mechanism for CH₄ to survive the main combustion and post-combustion process and to emit from the engine as unburned CH₄. The tools and approaches needed to conduct the instantaneous ROP analysis in CFD model will be developed. The following are the main tasks of the proposed research:

- 1) To validate a CFD model capable of simulating the combustion process and exhaust emissions from a NG-diesel dual fuel engine;
- 2) To develop a post-processing tool capable of calculating, analyzing, and visualizing the instantaneous ROP data in a CFD model.
- 4) To investigate the NO₂ formation mechanism in a NG-diesel dual fuel engine;
- 5) To investigate the CO formation mechanism in a NG-diesel dual fuel engine;
- 6) To explore the mechanism for CH₄ to survive the main combustion process and post-combustion oxidation process in a NG-diesel dual fuel engine;
- 7) To optimize the pilot fuel injection strategy aiming to minimize CH₄ emissions

from a NG-diesel dual-fuel engine.

Chapter 2 Literature Review

2.1 NG-diesel dual fuel engine

When burned in CI dual fuel engines, NG is usually fumigated into intake mixture, which forms a homogeneous NG-air mixture during the intake and early compression stroke. At the end of the compression stroke, a pilot of diesel fuel is injected directly into the hot NG-air-diluents mixture and serves as an ignition source. Before the injection of pilot diesel fuel, gaseous fuels have been mixed well with air and compressed to high pressure and high temperature, but usually not high enough to initiate the auto-ignition process of the NG. After being injected into the hot bulk mixture, the pilot diesel is in turn atomized, vaporized, mixed with the hot NG-air mixture, reacts with O_2 , interacts with NG, and ignited through auto-ignition. The energy released by the combustion of pilot diesel serves as an ignition source for the gaseous fuel. Detailed description of dual fuel engines combustion process can be found in the literature [3].

Compression ignition dual fuel combustion has been recognized as an attractive combustion mode for its potential of burning gaseous fuels at high thermal efficiency comparable to diesel engines and the reduced emissions of PM and NO_x [9-11]. However, the operation of NG-diesel dual fuel engine has been criticized for its excessive emissions of unburned CH₄, and CO, the incomplete combustion product of unburned CH₄, and also possible diesel fuel. The experimental research on NO_x emissions from dual fuel engines

[12, 13] reported the significant impact of the addition of NG and hydrogen (H_2) on NO_2 emissions from dual fuel engines. Extensive experimental research has been conducted to examine the factors affecting the ignition delay, combustion process, and the emissions of CH_4 , CO, NO_x and NO_2 from dual fuel engines [9-13].

2.2 CH_4 emissions from NG-diesel dual fuel engine

The CH_4 emitted from NG-diesel dual fuel engines is a waste of fuel and contributes to the emissions of GHG [14-16]. The research on CH_4 emissions at the early stage was conducted using single cylinder diesel engines converted to operate on NG-diesel dual fuel mode. For example, Karim et al. [17, 18] experimentally investigated the CH_4 emissions from a single-cylinder diesel engine converted to operate on NG-diesel dual fuel mode especially at low load operation. The impact of engine load, the CH_4 concentration fumigated into the intake mixture, and mass of diesel fuel injected in each cycle on the emissions of CH_4 and CO were experimentally measured. The potential of CH_4 and CO emissions and possible solutions in dual fuel engines especially at low load were reported [17, 18]. The research conducted in the past decades have investigated the detailed impact on CH_4 emissions of engine operation speed [19, 20], load [15, 21], substitution ratio [19, 22], exhaust gas recirculation (EGR) [22], NG fumigated into the intake manifold [23], and the amount of diesel fuel injected in each cycle [24]. For example, Gatts et al. [16] investigated the impact of engine load and the

volumetric ratio of NG fumigated into the intake mixture on CH₄ emissions from a heavy-duty (HD) diesel engine converted to operate on NG-diesel dual fuel mode. The emissions of CH₄ and CO, and fuel flow rate data was further processed to derive the combustion efficiency of CH₄ with the following assumptions: (1) the CH₄ emitted from the dual fuel engine was that added into the intake mixture; and (2) the CO emissions above that of pure diesel operation was due to the incomplete combustion of CH₄ while disregarding the possibility of the incomplete combustion of diesel and other hydrocarbons in NG. The lowest combustion efficiency observed at 10% load operation was about 65%. The maximum combustion efficiency observed at 70% load was about 95%, comparable to the combustion efficiency of SI NG engines. It was evident that the improvement of CH₄ combustion efficiency of dual fuel engines at low load would be one of the key challenges for the wide application of dual fuel engines. There is increasing recent interest in examining the impact of pilot fuel injection timing and injection pressure on combustion process and exhaust emissions [25-29] for NG-diesel dual fuel combustion mode.

Numerous researchers have examined the combustion process of dual fuel engines and the mechanisms for CH₄ to survive the combustion process and slip through the dual fuel engine. For example, Karim [3] classified the energy release rate of dual fuel combustion into three modes including: (1) the ignition of diesel fuel; (2) the concurrent combustion of diesel and NG presented within the diesel spray plume, (3) the combustion

of diesel free NG-air mixture. Liu et al. [12] discussed the pathways for CH_4 to be consumed in a HD dual fuel engine. These include: (1) the concurrent combustion of CH_4 with diesel fuel within the diesel spray plume; (2) the consumption of CH_4 by the propagating flame initiated by pilot diesel when CH_4 -air mixture is flammable; (3) the post combustion oxidation of CH_4 that survived the main combustion process but later on mixed with the hot combustion products. The CH_4 that survived the main combustion process but did not get an opportunity to mix with the hot combustion products would be highly likely to slip through the combustion chamber emit from the engine as unburned CH_4 . This was supported by the experimental data reported in the literature. For example, Dronniou et al. [30] investigated the combustion process of a dual fuel engine using a single-cylinder optical research engine which was typical of modern, light-duty diesel engines. A high-speed digital camera recorded time-resolved combustion luminosity and an intensified charge-coupled device camera was used for single-cycle OH^* chemiluminescence imaging. The propagation of the turbulent flame in diesel fuel free bulk gas was observed when the NG-air mixture was richer than the lean flammability limit [30, 31]. However, the NG-air mixture leaner than the flammability limit was not able to support the propagation of the flames initiated by the pilot diesel fuel [31]. The combustion process of the dual fuel engine was controlled by the mixing processes of the pilot fuel with the premixed charge (i.e. no flame propagation or bulk ignition). The consumption of the premixed charge of NG-air-residual gas becomes a significant challenge that led numerous researchers to explore approaches of optimizing pilot

injection settings (e.g. pilot injection quantity, timing, rail pressure and/or multiple pulse injection strategies) especially when the premixed charge was very lean. However, there is no research examining the mechanism for CH_4 to survive the combustion process of dual fuel engines. It is very difficult to identify the mechanism experimentally for CH_4 to survive the main combustion process.

2.3 CO emission from NG-diesel dual fuel engine

The CO emitted from internal combustion engines is an incomplete combustion product of hydrocarbon (HC) fuel [32]. In theory, CO can be formed in rich mixtures due to the lack of oxidant or in lean mixtures due to lower temperature. CO can also be formed during the post combustion oxidation process of HC which survived the main combustion stage. The CO emissions from both CI diesel engines and SI gasoline engines have been recognized as one of the key pollutants [33].

The research on the emissions from NG-diesel dual fuel engines reported a significant impact of the NG addition on CO emissions, especially at low load [15, 16, 19, 20]. For example, Gatts et al. [16] experimentally investigated the effect of NG/air ratio and engine load on CO emissions from a HD NG-diesel dual fuel engine. The increased addition of NG at medium (50%) to high (100%) load first increased, but then decreased CO emissions. Overall, NG-diesel dual combustion emitted more CO than diesel-only operation. The CO emissions at low load (10%) were significantly higher than at medium

and high loads and monotonically increased with the increased addition of NG. Similar CO emissions trends were also reported by other researchers [15, 19, 20]. Numerous experimental studies reported the effect of diesel fuel quantity and injection timing on CO emissions from NG-diesel dual fuel engines [26, 34-36]. For example, Liu et al. [26] experimentally studied the effect of pilot fuel quantity on the emission characteristics of a NG-diesel dual fuel engine. Zhang et al. [36] experimentally investigated the variation of CO emissions with changes in numerous operating parameters including engine speed, diesel fuel rail pressure, and diesel injection timing. As expected, the CO emissions from dual fuel engines were higher than that from traditional diesel engines.

Some studies have been conducted to reduce CO emissions from dual fuel engines. Wang et al. [37] investigated the effect of combustion chamber geometry on HC and CO emissions from a NG-diesel dual fuel engine. The results showed that the optimization methodology based on the Kriging meta-model and the optimized Latin hypercube sampling strategy could reduce HC and CO emissions by 56.47% and 33.55%, respectively. Dahodwala et al. [38] reported that the CO emissions could be reduced by the multi-pulse pilot fuel injection strategies. Similar observations were reported by Ishiyama et al. [39]. Abdelaal and Hegab [21] reported that the CO emissions can be slightly reduced when moderate EGR was applied. Literature review suggests that the operating condition has a significant influence on CO emissions from NG-diesel dual-fuel engines. The complex interactions among these parameters including

combustion chamber geometry, injection, and EGR make it very difficult to experimentally optimize NG-diesel dual fuel engine and to minimize CO emissions. This makes it necessary to better understand the CO formation and consumption chemistry in NG-diesel dual fuel engines.

Numerical simulation has been recognized as a viable method to derive the CO formation and consumption mechanism during the combustion process. Numerous numerical studies have been performed to reveal the fundamental mechanism of CO formation and consumption using zero-dimensional (0D) models with the oxidation process of hydrocarbon simulated using detailed chemical kinetics mechanisms [40-42]. For example, Jun et al. [41] simulated the CO formation and consumption in a CI engine operated on the homogeneous charge compression ignition (HCCI) mode. The mass of CO formed during the early combustion process started to reduce when the in-cylinder gas temperature reached about 1200K. The CO was completely oxidized to CO₂ when the temperature reached about 1500K. Bhave et al. [40] investigated the source of CO formed in an HCCI engine using an integrated SRM-based engine cycle model. It was observed that the formation of CO was affected by fluid-wall interactions, wall temperature, and the mixing between the hot combustion products and cold air-fuel mixture. Sjöberg et al. [42] examined the oxidation of CO in a lean burn HCCI engine using a single-zone model and reported that 1500K was necessary for the complete oxidation of CO to CO₂, which was consistent with that reported by Jun et al. [41].

The formation of CO and its oxidation in CI engines have also been numerically simulated using three-dimensional (3D) CFD models coupled with chemical kinetics mechanisms [43-53]. For example, Yang et al. [50] numerically investigated the CO formation characteristics of a gasoline-diesel dual-fuel engine using a KIVA-CHEMKIN model. The results showed that for highly-premixed compression ignition combustion condition, the CO trapped near the cold wall made a notable contribution to CO emissions. For low-temperature combustion (LTC) mode, CO was mainly formed near the cylinder axis and spray plume. An et al. [43] studied the emissions characteristics of a diesel engine fueled with diesel and biodiesel mixture. The simulation results showed that both the engine load and biodiesel blend ratio had a remarkable impact on CO emissions. However, most numerical studies on CO formation using CFD models presented the distribution of key parameters such as CO, temperature, and ER in cylinder without examining the contribution of reactions to the formation and consumption of CO [44-49, 51-53], which limit the understanding of CO combustion mechanism in NG-diesel dual fuel engine. Most of the analysis of the ROP of key species was conducted using 0D models as the platform. In comparison, the research on the chemical kinetics process associated with CO formation and consumption using 3D CFD model is relatively limited.

2.4 NO₂ emissions from NG-diesel dual fuel engine

The NO_x emitted from diesel engines consists of nitric oxide (NO) and NO₂. Although NO₂ was reported by Boezen, et al. [54] as a respiratory irritant to human health, especially to children with bronchial hyper-reactivity, the study of NO₂ emissions from diesel engines is limited because NO₂ emissions account for only a very small proportion of NO_x emissions, especially at medium to high load.

The recent research on NO_x emissions from NG-diesel dual fuel engines reported a significant impact of the addition of NG to intake mixture on NO₂ emissions, especially at low load [12]. For example, Liu et al. [12] experimentally investigated the NO₂ emissions from a HD diesel engine fumigated with NG or H₂. The NO₂ emissions from the diesel engines were affected by the load of engine operation. For example, the NO₂/NO_x ratio of diesel engine was found to vary from 5% (70% load) to 15% (10% load). The addition of NG to the diesel engine significantly increased NO₂ emissions and NO₂/NO_x ratio. The maximum NO₂ emissions from the dual fuel engine were about three (at 70% load) to five (at 10% load) times of those observed with diesel only operation [12]. A similar phenomenon has been reported with the addition of H₂ [12, 13, 55-57]. Although numerous studies reported the significant impact of premixed gaseous and liquid fuels on NO₂ emissions from CI dual fuel engines, the research on the fundamental knowledge of the NO₂ formation reaction pathway in dual fuel engines has not been reported. The development of approaches aiming to control NO₂ emissions from dual fuel

engines requests the detailed investigation of the NO₂ formation reaction pathway.

Previous fundamental research on NO_x formation has investigated the formation of NO at high temperature and its conversion to NO₂ promoted by hydrocarbons [58-61]. For example, NO₂ can be produced through the reaction $\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO}$, where $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \dots, \text{C}_n\text{H}_{2n+1}$ [61]. In the past decades, the NO₂ formation mechanism was further revealed by examining the NO–NO₂ conversion reaction: $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$. For example, Hori et al. [58] numerically and experimentally examined the factors affecting the NO–NO₂ conversion including hydrocarbon type, residence time, and reaction temperature. It was concluded that the NO–NO₂ conversion was only observed at a relatively low temperature range from 650 to 1000K. Such a conversion was dominated by the capability of hydrocarbons in producing reactive radicals such as OH and O. Mueller, et al. [60] experimentally and numerically studied the NO to NO₂ conversion in a flow reactor at a low-temperature range (750-1100K). The NO to NO₂ conversion was affected by the pressure and stoichiometry of the air/fuel mixture. Kyne, et al. [59] examined the NO to NO₂ conversion in counterflow diffusion flames. The examination of the ROP and the sensitivity analysis indicated that the NO to NO₂ conversion was more sensitive to the concentrations of CO₂, CO, hydrocarbons, NO, and NO₂ than to the initial pressure. However, little fundamental research on the NO₂ reaction pathway in NG-diesel dual fuel engines has been reported.

2.5 Limitation of current commercial CFD software

Commercial CFD models have been widely used to predict the combustion process of diesel engines featuring diffusion combustion. The pressure and temperature, and distribution of species in cylinder and their variations with changes in crank angle can be predicted and plotted. However, most of the current commercial CFD models cannot be directly used to explore the chemical kinetics process, and to identify the key reactions and species dominating the formation and destruction of species such as NO_x. The examination of the key reactions and species dominating the formation and destruction of key species requires the calculation of the instantaneous ROP of each species in each cell. However, it is very difficult for the current commercial CFD models to export the instantaneous ROP of each species. For example, the instantaneous ROP data calculated at each computational cell is a $m \times n$ sparse matrix for a chemical kinetics mechanism with m reactions and n species when calculated using CHEMKIN [62]. Thus, it requires significantly large computational memory for the CFD model to export the ROP data, especially for direct numerical simulation (DNS) and large eddy simulation (LES) models, which generate significantly large numbers of computational grids. This may be the reason that the instantaneous ROP data is calculated in CFD models, but usually not exported for post processing. This makes the past analysis of CFD simulation focused mainly on the spatial distribution of important parameters, such as temperature and key species. However, with the appropriate analysis method, the ROP

data in a CFD model can be derived and applied to investigate the effect of the instantaneous local species concentrations and thermal properties on the chemical kinetics process. This is very important for further understanding the combustion process, formation of pollutants in cylinder, and key reactions and species dominating the distinct combustion stage such as ignition delay. Therefore, the approaches and tools deriving the instantaneous ROP data and its further analysis in a CFD model is essential.

Chapter 3 Experimental Setup and Numerical Model

Validation

This chapter presents the experimental setup and validation of numerical model in this research. The experimental data in this research are provided by Tianjin University (Engine I) and National Research Council (NRC) Canada (Engine II).

3.1 Engine I

The experiment of Engine I was performed by State Key Laboratory of Engine (SKLE) in Tianjin University, China. It was a turbo-charged, HD six-cylinder diesel engine, with a compression ratio of 16.8, bore of 123 mm, and stroke of 145 mm. The diesel injector has 8 evenly-distributed injection holes of 0.16 mm diameter. The injection spray angle was 75°. This engine was converted to operate on NG-diesel dual fuel with NG injected into the intake manifold using a multi-point port injection system. The pilot diesel was directly injected into the cylinder at 160 MPa using a common-rail fuel injection system. The detailed specifications of the engine, dynamometer, data acquisition system, and exhaust gas analyzer can be found in the literature [63]. Table 3.1 shows the engine operation parameters tested and simulated in this research. The indicated and brake thermal efficiency measured were 43.51% and 31.91%, respectively.

Table 3.1 Operation parameters of Engine I [63]

Engine speed	1420 rpm
Engine load	4.9 bar BMEP*
Diesel Injection Pressure	160 MPa
Diesel Injection Timing	6° CA BTDC
Diesel Injection Duration	3.50 °CA
Intake Temperature	300 K
Intake Pressure	1 atm
EGR Rate	20%
Diesel Fuel Injected	20.0 mg/cycle
CNG Fuel Added	38.0 mg/cycle
Vol. Fraction of CH ₄ in Intake Mixture	3%

BMEP: Brake mean effective pressure

BTDC: Before top dead center

3.2 Engine II

The experiments of Engine II applied in this research were conducted by National Research Council (NRC) Canada. The experiments were conducted in a single cylinder, 4-valve, Caterpillar diesel engine with a compression ratio of 16.25, a bore of 137.2 mm, and a stroke of 165.1 mm. The engine test cell was configured to simulate the operation of a turbocharged HD diesel engine. The detailed specification of the engine, dynamometer, data acquisition system, and exhaust gas analyzer can be found in the literature [64]. The engine was converted by the NRC to operate in the NG-diesel dual fuel mode. In this research, NG was added to the intake air using a port-fuel NG injector installed between the intake surge tank and intake valve. The pilot diesel was directly

injected into the cylinder using a common-rail fuel injection system at 525 bar. The diesel injector has 6 injection holes of diameter 0.23 mm and is installed at the center of the cylinder head. The injection spray angle was 65°. In this research, the engine was operated at an engine speed of 910 rpm, and a BMEP of 4.05 bar, a typical low load operation condition featured with low CH₄ combustion efficiency. The gaseous fuel used was pipeline NG consisting of 95.80% CH₄, 2.34% ethane, 0.19% propane, 0.98% N₂, 0.64% CO₂ and traceable high hydrocarbons [64]. Tables 3.2 and 3.3 show the specification of this engine and the operating conditions simulated in this study, respectively. Table 3.4 shows the mass flow rate of diesel fuel and NG at each case tested. The energy contribution of NG was reported as the ratio of energy of NG relative to total energy. For example, 25NG represents a case with 25% energy provided by NG and 75% energy provided by pilot fuel.

Table 3.2 Engine specification of Engine II

Parameter	Value
Basic engine model	Caterpillar 3401
Parent engine	Caterpillar 3400 series
Number of cylinder	1
Bore x stroke	137.2 mm x 165.1 mm
Compression ratio	16.25:1
Displacement	2.44 liter
Number of valve	4
Combustion chamber type	Quiescent
Diesel fuel injection type	Direct injection
Diesel fuel injector	Ganser CRS AG
Natural gas injection type	Port injection
NG injector	AFS Gs60 injectors
Maximum power output	74.6 kW (@2100 rpm)

Table 3.3 Engine Operation Parameters Engine II

Engine speed	910 rpm
Engine load	4.05 bar BMEP
Intake temperature	40 °C
Intake pressure	105 kPa
EGR Rate	0%
Diesel Injection pressure	525 bar
Injection timing	$-7^{\circ} CA ATDC$

Table 3.4 The mass of diesel and NG consumed each cycle at each case, Engine II

Cases Tested		Diesel fuel, mg/cycle	NG		
			Mass, mg/cycle	Vol. conc. in intake mixture	NG Contribution to total fuel energy
Case 1	0NG	66.2	0.0	0.00%	0%
Case 2	25NG	49.7	15.5	1.33%	25%
Case 3	50NG	34.8	32.2	2.72%	50%
Case 4	75NG	18.1	50.9	4.21%	75%

3.3 Computational model

The simulation model used is the 3D CFD software CONVERGE [65]. The diesel fuel chemistry was represented by n-heptane. The physical property of diesel fuel was represented by tetradecane ($C_{14}H_{30}$) to simulate the spray development, atomization, vaporization and the mixing of n-heptane with air. NG was represented by CH_4 . The fuel chemistry used was a reduced PRF mechanism consisting of 41 species and 130 reactions (Appendix II) [66]. The NO_x mechanism (4 species and 12 reactions) from GRI chemistry [67] was added for the simulation of NO_x (Appendix III). Table 3.5 shows the list of sub-models applied for simulation, which had been validated by Yang et al. [50] for a gasoline/diesel dual fuel combustion study. The spray-wall interaction was simulated using an O'Rourke model [68]. The basic mesh size was 4 mm. An adaptive mesh generation method with up to 300,000 grids was applied. Figures 3.1 and 3.2 show an example of the mesh generated for Engine I and Engine II, respectively. The simulation started from the intake valve close (IVC) with the assumed homogeneous mixture of NG,

air, and residual gas and completed at the exhaust valve open (EVO). The pressure, temperature, and composition of the bulk mixture were calculated. The mass and concentration of the air-fuel mixture in cylinder were calculated using experimental data.

Table 3.5 List of sub-models used in the simulation

Phenomenon	Model	Reference
Spray-wall interaction	O'Rourke	[68]
Spray breakup	Hybrid KH-RT	[69]
Droplet collision	NTC collision method	[70]

Figure 3.1 Example of mesh generated for Engine I.

Figure 3.2 Example of mesh generated for Engine II.

3.4 Model validation

The Converge CFD model with PRF chemistry was validated against experimental data measured in two engines. Figure 3.3 shows the model validation for Engine I. The simulated cylinder pressure and heat release rate (HRR) are found to agree well with experimental data measured at 1420 rpm and BMEP of 4.9 bar.

Figure 3.3 Model validation against cylinder pressure and heat release rate at 4.9 bar BMEP and 1420 rpm, measured in [63].

Figures 3.4 to 3.8 show the model validation for Engine II. As shown in Figure 3.4, the simulated cylinder pressure and HRR agree well with experimental data measured with NG contributing up to 75% of the total energy consumed. The model was also able to reasonably predict the trend of NO_x, CO and CH₄ emissions, as well as NO₂ and NO₂/NO_x ratio, as shown in Figures 3.5 and 3.6. The quantitative difference between the measured and simulated emissions might be due to the imperfect pilot fuel spray model, the representation of diesel fuel chemistry using n-heptane, the reduced fuel chemistry. The simulated CH₄, CO, NO, NO₂, NO_x emissions calculated at EVO other than exhaust gas may also contribute to the difference between the simulated CH₄ and CO emissions and experimental data. Although the CFD model over-predicted the CH₄ emissions and under-predicted the CO emissions (shown in Figure 3.5). The predicted sum of the mass of CO and CH₄ at EVO agreed well with the experimental data, as shown in Figure 3.7. It is evident that the CFD model coupled with a reduced fuel

chemistry is able to reasonably predict the percentage of CH_4 burned in this dual fuel engine.

Figure 3.4 Comparison of the simulated cylinder pressure and HRR with experimental data measured at 0NG, 25NG, 50NG, and 75NG, respectively.

Figure 3.5 Comparison of the simulated CO, NOx and CH₄ emission with experimental data.

Figure 3.6 Comparison of the simulated NO₂, NO emissions and NO₂/NOx mass ratio with experimental data.

Figure 3.7 Comparison of the sum of the simulated CH₄ and CO with experimental data

Figure 3.8 shows the percentage difference between the predicted and measured peak cylinder pressure (PCP) and CO+CH₄ emissions with experimental data. The maximum difference between the predicted and measured PCP is 2.5%. The maximum difference between the measured and predicted emissions of CO+CH₄ is 12.0%, which is observed at 75NG. The difference between the predicted and measured CO+CH₄ emissions in the other three cases is relatively low (within 7%). It is evident that the CONVERGE CFD model with a reduced PRF mechanism is able to reasonably simulate the combustion process, and the emissions of CH₄, CO, and NO₂ in the two dual fuel engines tested.

Figure 3.8 Difference between the predicted and measured CO+CH₄ emissions and peak cylinder pressure

3.5 Laminar flame speed for unburned methane

Figure 3.9 shows the temperature of unburned CH₄ for after 60 °CA ATDC for 25NG, 50NG, and 75NG cases. The increased temperature with higher NG substitution ratio is due to the slow oxidation and chemical heat release in CH₄/air mixture. The average temperature of these three cases are 593K, 681K, and 948K, respectively.

Figure 3.9 Temperature of unburned CH₄ for after 60 °CA ATDC for 25NG, 50NG, and 75NG cases

Figure 3.10 Laminar flame speed of CH₄/air mixture, pressure: 4.05bar, equivalence ratio: 0.1 to 1, temperature: 593K, 681K, 948K.

Figure 3.10 shows the laminar flame speed of CH₄/air mixture, the calculation is conducted under pressure of BMEP with 4.05 bar, equivalence from 0.1 to 1, and temperature of 593K, 681K, 948K, respectively. As shown in Table 3.6, the mole fraction of CH₄ in the intake mixture at 75NG is 4.21%, with the equivalence ratio of 0.419. It can be observed in Figure 3.10 that the laminar flame speed of CH₄/air mixture is about 100 cm/s at 948K and equivalence ratio of 0.4, which corresponds to 0.018 cm/°CA. This indicates that the flame propagation speed is significantly low so that can be neglected during the post combustion stage with the operation condition selected in this research.

Table 3.6 Equivalence ratio of NG-air mixture

Case	Vol. conc. of NG	ER
25NG	1.33%	0.128
50NG	2.72%	0.266
75NG	4.21%	0.419

Chapter 4 The Development of Post-Processing Tool

This chapter presents the development of the post-processing tool for the calculation, analysis, and visualization of instantaneous ROP data using the data exported by CONVERGE, and the important definitions that are applied in this research.

4.1 The Development of post processing tool

The temperature, pressure, and species concentrations at each computational cell calculated using CFD model are exported to a 'column format' file. A MATLAB code is developed to read the temperature, pressure and species concentrations in 'column format' file and to transfer them to CHEMKIN [62] for ROP data calculation. Each computational cell is treated as a WSR during CHEMKIN calculation process. The calculated ROP data includes 1) The creation/destruction rate of each species in each cell; 2) The forward/reverse reaction rate of all reactions; 3) The contribution of each reaction to the production rate of a species, and 4) The chemical heat release of each reaction. Table 4.1 shows the number of parameters examined with the PRF mechanism [66] coupled with the CFD model, and the key subroutines in the CHEMKIN package that are applied to calculate these parameters. There are 1051 ROP variables to be calculated in each cell for the PRF mechanism [66]. The calculated ROP data are analyzed and visualized by MATLAB code. Figure 4.1 shows the flowchart of CONVERGE-SAGE model and post-processing procedure. The number of contribution of each reactions to

production rate of a species is counted from the sparse stoichiometric coefficient matrix.

The detailed equations for ROP calculation can be found in Appendix I. The CHEMKIN source code to calculate the instantaneous ROP at one cell is given in Appendix IV.

Table 4.1 Number of calculated ROP variables with reduced PRF mechanism [66], and the key subroutines in CHEMKIN package to calculate the instantaneous ROP data.

Variable	numbers	subroutine
Creation/destruction rate of all species	2×45	CKCDXP
Forward/reverse reaction rate for each reaction	2×142	CKKFKR
The contribution of each reaction to production rate of a species	535	CKCONT
Chemical heat release for each reaction	142	CKHML
Total variables	1051

Figure 4.1 Flow chart of CONVERGE-SAGE model calculation, and post-processing tool presented in this research.

4.2 Important definitions for this research

Calculation of progress variable

The progress variable (pv) of the i^{th} reaction is calculated by equation (4.1) [71]:

$$q_i = k_{f_i} \prod_{k=1}^K X_k^{v'_{ki}} - k_{r_i} \prod_{k=1}^K X_k^{v''_{ki}} \quad (4.1)$$

where v_{ki} is the stoichiometric coefficients, superscript ' indicates forward stoichiometric coefficients and '' indicates reverse stoichiometric coefficients; i indicates the index of i^{th} reaction, while k indicates index of the k^{th} species; X_k is the molar concentration of the k^{th} species; k_{f_i} and k_{r_i} are the forward and reverse reaction rate constants (RRC) of the i^{th} reaction, respectively, calculated by Arrhenius expression. The examination of RRC and species concentration helps to better understand the key factors dominating the pv.

Representative creation/destruction reaction

Among all the reactions involved in the i^{th} species creation/destruction in each computational cell, there exists a reaction that has the largest creation/destruction rate. Such a reaction has the largest contribution to the creation/destruction of the i^{th} species and is defined as the representative creation/destruction reaction (RCR/RDR).

Representative endothermic/exothermic reaction

Among all the reactions involved in the chemical heat release in each

computational cell, there exists a reaction that has the largest contribution to the instantaneous endothermic/exothermic effect and is defined as representative endothermic/exothermic reaction (RNR/RXR). This research will examine the RNR/RXR in n-heptane spray during LTC and auto-ignition process.

Instantaneous species destruction pathway

In this research, the instantaneous species destruction pathway (ISDP) is analyzed by examining the instantaneous contribution of each reaction to the destruction of a species using equation (4.2).

$$\beta_{d,i,j} = \frac{\omega_{d,i,j}}{\sum \omega_{d,i,j}} \quad (4.2)$$

Where: $\omega_{d,i,j}$ represents the destruction rate of i^{th} species by j^{th} reaction, $\sum \omega_{d,i,j}$ is the destruction rate of i^{th} species. $\beta_{d,i,j}$ is the normalized contribution of the j^{th} reaction to i^{th} species destruction.

Calculation of ER

The ER at each computational cell is calculated using equation (4.4) [65]:

$$Phi = \frac{2 \sum N_i \eta_{C,i} + 0.5 \sum N_i \eta_{H,i}}{\sum N_i \eta_{O,i}} \quad (4.4)$$

Where N_i is the number of moles of the i^{th} species in each cell, $\eta_{C,i}$, $\eta_{H,i}$, $\eta_{O,i}$ are the number of carbon (C), hydrogen (H) and oxygen (O) atoms in each species, respectively. In this research, the elements in H₂O and CO₂ are not considered in the ER calculation.

Calculation of mixture fraction

The mixture fraction is calculated by [65]:

$$Z = \sum_{i=1}^{n_s} \frac{N_{C_i} W_C Y_i}{W_i} + \sum_{i=1}^{n_s} \frac{N_{H_i} W_H Y_i}{W_i} \quad (4.5)$$

where i is the species index, n_s is the number of species, N_{C_i} and N_{H_i} are the number of carbon and hydrogen atoms, respectively, in i th species, W_C and W_H are the molecular weights of carbon and hydrogen, respectively, Y_i is the species mass fraction, and W_i is the molecular weight of the i th species. The mixture fraction is featured with element mass conservation and applied to identify the concentration of diesel fuel mixes with NG/air mixture and their combustion products in dual fuel combustion mode.

Calculation of spray momentum

The momentum of spray is calculated by:

$$M = \sum mass \times velocity \quad (4.3)$$

In this research, the computational cells where the mixture fraction is larger than 0.01 is identified as the ‘spray region’ which is applied to identify the diesel fuel injected since the mixture fraction is characterized with element mass conservation. The comparison of spray momentum provides useful information to quantify the in-cylinder flow caused by high pressure injection.

4.3 Numerical method applied in this research

Quasi-homogeneous constant volume model

A quasi-homogeneous constant volume (QHCV) model is developed to simulate the formation of NO₂ in a bulk gas consisting of NO₂, NO, O₂, CH₄, etc. The QHVC model is applied to simulate the chemical reactions in a selected region covering 95% of NO₂ formed in this engine. The initial inputs of the QHVC model are the average temperature and mixture compositions calculated using Ensight software, a tool processing the output data of the CONVERGE software. The rates of formation and consumption of the key species are calculated by calling CHEMKIN subroutines.

Reaction rate analysis using an integration method

In this study, the reaction path dominating NO₂ formation in a NG-diesel dual fuel engine is investigated through analyzing the species conversion ratio, the contribution of each reaction to the formation and consumption of a specific species. This is performed by dividing the reaction rate of the *i*th species in the *k*th reaction by the overall reaction rate of the *i*th species in all reactions involved.

The conversion ratio from the *i*th species to the *j*th species is:

$$\alpha_{i \rightarrow j} = \frac{\int \omega_{i \rightarrow j}}{\sum (\int \omega_{i,k})_{con}} \quad (4.6)$$

Where: ω is the reaction rate of a species; *i, j* represent the species index; $\omega_{i \rightarrow j}$ is the rate of reaction through which the *i*th species is converted to the *j*th species; *con*

represents consumption; $\int \omega_{i \rightarrow j}$ is integration of the conversion ratio from the i^{th} to j^{th} species over the time period from the start of reaction to 90% conversion from NO to NO₂; $\Sigma(\int \omega_{i,k})_{con}$ represents the sum of $\int \omega_{i \rightarrow j}$ for all reactions.

The contribution of the k^{th} reaction to the consumption of the i^{th} species is:

$$\beta_{i,k} = \frac{\int \omega_{i,k,con}}{\Sigma(\int \omega_i)_{con}} \quad (4.7)$$

Where: $(\int \omega_i)_{con}$ is the integration of the rate of reaction which consumed the i^{th} species over the time period from the start of reaction to the end of reaction or calculation (90% conversion from NO to NO₂ in this research); $\Sigma(\int \omega_i)_{con}$ is the sum of the integrated consumption rate of the i^{th} species in all reactions involving the consumption of the i^{th} species.

The contribution of the k^{th} reaction to the production of the i^{th} species is:

$$\gamma_{i,k} = \frac{\int \omega_{i,k,pro}}{\Sigma(\int \omega_i)_{pro}} \quad (4.8)$$

Where: pro represents the production of species; $(\int \omega_i)_{pro}$ represents the integration of the rate of reaction which produced the i^{th} species; $\Sigma(\int \omega_i)_{pro}$ is the sum of the integrated production rate of the i^{th} species in all reactions involving the production of the i^{th} species.

Chapter 5 CH₄ Combustion and Emissions from a NG-Diesel Dual Fuel Engine

This chapter presents a numerical study on the combustion process of a NG-diesel dual fuel engine using a CFD model CONVERGE coupled with a reduced PRF mechanism. This is most likely the first attempt to visualize the spatial distribution of CH₄ in dual fuel engines using CFD. The objective of this research is to numerically simulate the CH₄ combustion process, especially the CH₄ present outside the pilot spray plume, quantify the CH₄ combustion in each combustion stage, and visualize the spatial distribution of CH₄ in cylinder. The experimental data of Engine II is applied.

5.1 CH₄ combustion at main combustion stage.

Figure 5.1 shows the simulated evolution of n-heptane spray, the distribution of temperature, ER, and CH₄ in a cut-plane in the middle of the injection spray for the 25NG case. In this research, the ER is calculated using the concentration of fuel and O₂ without accounting for CO₂ and H₂O formed through the combustion of the pilot and CH₄. With the development of the spray plume, the ER within the n-heptane spray plume is found to first gradually increase accompanied by the injection of pilot fuel but then decrease due to the atomization and vaporization of n-heptane and mixing with the CH₄-air mixture. The continued increase in ER within pilot fuel spray, especially after the consumption of n-heptane, is due to the consumption of O₂ during the combustion process of n-heptane

and CH_4 within the spray plume. The concentration of CH_4 and the temperature inside the spray are noted to increase from -2.5 to 0.1° crank angle (CA) after top dead center (ATDC). This is due to the formation of CH_4 during the oxidation of n-heptane. Accordingly, not all of the CH_4 present outside the n-heptane spray plume can be burned due to the lack of flame propagation. With the combustion of CH_4 in the rich mixture featuring $\text{ER} > 1$, the ER value would further increase due to the consumption of O_2 . In comparison, the ER of the lean fuel mixture ($\text{ER} < 1$) would gradually decrease to zero (complete combustion) with the consumption of fuel as there is excess O_2 present. The temperature distribution shows that ignition is first observed at the periphery of the n-heptane plume where n-heptane and methane-air mixture are sufficiently mixed.

Figure 5.1 The evolution of spray plume, distribution of temperature, equivalent ratio, and molar fraction of CH_4 during n-heptane injection and ignition process. Case: 25NG. From top to bottom: -2.5° , 0.1° , 4.3° CA ATDC.

Figure 5.2 shows the variation of cylinder pressure, HRR, and average molar

fraction of n-heptane, CH₄, CO, OH, CH₂O and H₂O₂ with the change in CA for 25NG case. N-heptane evolution endures a two-stage consumption representing the transfer from the low temperature oxidation to the negative temperature coefficient region. The production of OH is accompanied by the consumption of n-heptane after about -2.3° CA ATDC, which is recognized as the start of high temperature combustion (HTC) of the premixed n-heptane/air/ CH₄ mixture. Radicals such as CO, CH₂O, and H₂O₂ are found to gradually increase prior to the start of HTC following the injection of pilot fuel. The premixed combustion starts from -2.3° CA ATDC and lasts until 1° CA ATDC during which the n-heptane-CH₄-air mixture at the periphery of the n-heptane plume burns. The diffusion combustion of n-heptane starts at 1° CA ATDC and lasts until 4.5° CA ATDC as indicated by the complete consumption of n-heptane. During this period, the production of the intermediate combustion products such as CO is accompanied by the production of CH₄. The H₂O₂ and CH₂O are found to gradually decrease to very low values with the consumption of n-Heptane. CH₄ is mainly consumed during the late diffusion combustion after the completion of n-heptane combustion. The continued release of heat after complete consumption of n-heptane is due to the combustion of n-heptane combustion products and CH₄. The oxidation of CH₄ after the complete combustion of n-heptane is accompanied by high concentrations of CO and OH. In comparison, the concentrations of CH₂O and H₂O₂ observed after the complete combustion of n-heptane is relatively small compared with their peak values.

Figure 5.2 Variation of cylinder pressure, heat release rate, and the molar fraction of n-Heptane, CH₄, CO, OH, H₂O₂, and CH₂O with changes in CA. Case: 25NG.

The combustion of CH_4 and geometric location of the survived CH_4 within the bulk gas are examined by evaluating the distribution of temperature (over 1800K representing region involving combustion of n-heptane, and CH_4), combustion products such as CO_2 , concentration of O_2 and CH_4 in the bulk gas. Figure 5.3 shows the velocity field from injection and hot combustion products represented by the region where $T > 1800\text{K}$. It should be noted that the color of the arrow represents the value of the velocity of bulk gas movement. The momentum of bulk gas created by the spray jet, piston movement, and combustion pushed the hot combustion products toward the unburned CH_4 -air mixture. The mixing between the hot combustion products and the cool CH_4 -air mixture increased the temperature of CH_4 and O_2 , leading to the oxidation of the unburned CH_4 . This contributed to the combustion of CH_4 present outside the pilot fuel spray plume and the oxidation of the intermediate combustion products such as CO originating from rich combustion products because O_2 was made available from the O_2 -rich CH_4 -air mixture. Accordingly, the combustion of CH_4 outside the spray plume is dominated by the mixing of the hot combustion products and the unburned CH_4 -air mixture. Such a process is controlled by the interaction among piston compression, the bulk gas movement triggered by the pilot fuel spray jet, and the expansion and diffusion of combustion products due to the increased temperature during combustion. The bulk movement triggered by the spray jet and the subsequent mixing of the hot combustion product with the cool CH_4 -air mixture, and oxidation of CH_4 gradually become weak, especially after the completion of the main combustion process. This slows down the

mixing of hot combustion products with the unburned mixture and the oxidation of CH_4 present outside pilot fuel spray plume.

Figure 5.3 The distribution of high temperature region ($T > 1500\text{K}$) and velocity field at 3, 10, and 15 °CA ATDC. 25NG

Figure 5.4 shows the spatial distribution of O_2 , CH_4 and temperature of bulk gas at about 20° CA ATDC representing the late diffusion combustion. The arrow vectors shown in the temperature distribution figure are the distribution of velocity representing the movement of bulk gas driven by the momentum of the pilot fuel, expansion of bulk gas due to combustion, and down-ward movement of the piston. The CH_4 concentration in the vacant region (no color) surrounded by the dark blue one (representing low CH_4 concentration) shown in the CH_4 distribution figure is extremely low, indicating the complete combustion of CH_4 . As shown in Figure 5.4, the velocity field of the bulk gas observed in the 25NG case is much stronger than that observed in the 75NG case. This is due to the higher momentum of the pilot fuel injected at 25NG than that at 75NG benefiting from the injection of more pilot fuel at 25NG than 75NG. Accordingly, the hot combustion products at 25NG are pushed further toward the cylinder head, the surface of

combustion chamber, touch the piston bowl surface and bounce back toward the centerline of the combustion chamber. In comparison, the injection momentum in the 75NG case is too weak for the pilot fuel to reach the piston bowl surface, so it drives the hot combustion products toward the piston top platform and the squish area, resulting in the consumption of CH₄-air mixture in a different region. The low O₂ concentration (dark blue and region without color surrounded by dark blue) shown in Figure 5.4 represents the region where the combustion of n-heptane is involved as the majority of O₂ has been consumed by combustion. This is supported by the high bulk mixture temperature observed. The medium O₂ concentration area (light-blue and green) represents the region where combustion/oxidation of CH₄ is involved or mixed with combustion products of pilot fuel. The CH₄ in this region is consumed during the post combustion oxidation process after being mixed with hot combustion products. The CH₄ concentrations in these two regions are extremely low as represented by the blue area. The region featuring a high concentration of O₂ and CH₄ represents the bulk gas where the oxidation of CH₄ has not been initiated or only partially oxidized. Plus, the addition of CH₄ affects the mass of pilot fuel injected, the development of the pilot fuel spray, atomization, mixing with the bulk gas, and combustion. This is confirmed by the distribution of unburned CH₄ in cylinder as shown in Figure 5.4. The addition of more NG increases the volume of the region with unburned CH₄, which is due to the decreased amount of injected diesel fuel. It is evident that the mixing of the hot combustion products with the unburned CH₄-air mixture to some extent dominates the consumption of CH₄ in the premixed CH₄-air

mixture without involving n-heptane.

Figure 5.4 the distribution of temperature and velocity, mole fraction of O_2 and CH_4 observed at 20 °CA ATDC. From top to bottom, case: 25NG, 50NG, and 75NG.

5.2 CH_4 oxidation at post combustion stage

The unburned CH_4 observed in the dual fuel engine after the completion of the main combustion process is located at a region away from the pilot fuel plume where the unburned CH_4 -fuel mixture has not had a chance to be mixed with the hot combustion products. Figure 5.5 shows the distribution of unburned CH_4 , the bulk mixture

temperature, and the velocity field in the interface region at 50 °CA ATDC representing a CA at which the CH_4 is consumed through the weak post combustion oxidation process. The hot combustion products are moving downward following the downward movement of the piston. In comparison, the driving force originating from the injection of the pilot fuel and early combustion become negligible. The heat release at this stage is very low due to the slow oxidation of CH_4 occurring at the interface between the hot combustion products and the relatively cool CH_4 -air mixture. This is due to the very slow mixing between the hot combustion products and cool mixture containing CH_4 . Plus, the temperature of the bulk gas in both the burned and unburned area is decreasing following the downward movement of the piston. As shown in Figure 5.5, the majority of CH_4 which survived at 50 °CA is present in the area far from the hot combustion products. The majority of CH_4 which survived at this point will eventually exit the cylinder as unburned CH_4 .

It is evident that the combustion of the pilot fuel, volumetric ratio of the pilot fuel injection spray plume or pilot fuel vapor relative to the total volume, the movement of the hot combustion products towards to unburned mixture, and its mixing with CH_4 -air mixture dominate the combustion of CH_4 in a dual fuel engine. The injection parameters including geometry of injector holes, number of injector holes, and injection angle, injection timing may play an important role in CH_4 emissions from NG-diesel dual fuel engines. This is consistent with experimental results observed in an optical engine [12,

31].

Figure 5.5 Distribution of the unburned CH₄, bulk mixture temperature, and velocity field in the interface at 50 °CA ATDC. From top to bottom, case: 25NG, 50NG and 75NG.

Figure 5.6 shows the distribution of CH₄ in-cylinder at EVO. In this research, the

CH_4 observed at EVO is reported as the emissions of the unburned CH_4 . The unburned CH_4 is mainly located at the n-heptane free region such as the center of the combustion chamber and boundary area around the cylinder liner, especially for the 50NG and 75NG cases. In comparison, the contribution of the boundary layer to total unburned CH_4 is found to increase with the increased amount of CH_4 added. The development of approaches and control strategies to reduce the emissions of the unburned CH_4 should focus on enhancing the combustion of CH_4 in the center of the combustion chamber, and on approaches capable of enhancing the mixing between the hot combustion products and cool CH_4 -air mixture.

Figure 5.6 Distribution of the unburned CH_4 in cylinder at EVO. From left to right, case: 25NG, 50NG and 75NG.

The simulated distribution of CH_4 and its variation with the combustion process is further processed to derive the percentage of CH_4 consumed in each stage. Figure 5.7 shows the percentage of CH_4 consumed during each stage and the percentage of CH_4 observed at EVO. The main combustion process consumed 43-53% of the CH_4 followed by 17-29% consumption during the post combustion oxidation process. The unburned CH_4 observed at EVO is about 27 to 35% of that added to the intake mixture at the simulated load. It should be noted that the combustion of CH_4 is affected by the concentration of CH_4 added, the volume of pilot fuel spray plume, the temperature of combustion products, and the mixing between the hot combustion products and the pilot fuel-free bulk mixture containing CH_4 . The mixing between the hot combustion products and pilot fuel-free bulk mixture containing CH_4 is dominated by the movement of the hot combustion products toward the cool CH_4 -air mixture. The movement of the hot bulk gas is initiated by the momentum of the pilot fuel directly injected into the cylinder, which is enhanced by the expansion of the combustion products due to the increased temperature during the combustion process, and guidance of the piston bowl. The interaction among pilot fuel injection spray, configuration of the combustion chamber, direction of piston movement, and combustion process dominate the mass transfer from the hot combustion products to the cold unburned CH_4 -air mixture.

Figure 5.7 CH₄ consumption during each stage after 99% n-heptane consumed.

5.3 Discussion regarding CH₄ emissions optimization

The simulation work conducted in this research reveals the combustion of CH₄ in a NG-diesel dual fuel engine, the important role of post-combustion oxidation in burning the CH₄ which survived the main combustion process, and the spatial distribution of the unburned CH₄ in-cylinder. The optimization of the engine aiming to enhance the combustion of CH₄ in a dual fuel engine should focus on the following aspects: (1) increasing the relative volumetric ratio of bulk gas mixed with vapors of the pilot fuel. This can be achieved through (i) modifying the design of the fuel injector such as increasing the size or volume of pilot fuel spray plume which can be achieved through the adjusting the spray angle, number of injection holes, diameter of injector holes, and injection pressure of pilot fuel; (ii) increasing the ignition delay time period to allow for enough time for the atomization, vaporization of the pilot fuel, and its mixing with bulk gas prior to the auto-ignition of the pilot fuel vapor. This can be achieved through optimizing fuel injection strategies such as using multiple-fuel injection pulse such as

adding a pre-pilot injection pulse prior to the main injection pulse of pilot fuel or using pilot fuel with slightly lower Cetane number. (2) Enhancing the movement of the hot bulk gas toward the cold unburned CH_4 -air mixture, especially the movement of hot combustion products toward the center of the cylinder, which requires a better design of the piston bowl geometry, increasing the swirl ratio of the intake system and the matching between fuel injection strategies and piston bowl geometry. The mixing of the combustion products with the unburned premixed mixture should occur early in the expansion process when the temperature of the hot combustion products is still sufficiently high to oxidize the unburned CH_4 .

5.4 Summary

A numerical study on the combustion of CH_4 in a NG-diesel dual fuel engine during the main combustion and post combustion process has been conducted. The spatial distribution of CH_4 in-cylinder and the consumption of CH_4 at each combustion stage are examined. Based on the CH_4 combustion and distribution data simulated at the engine speed of 910 RPM and load of 4.05 bar BMEP, the following conclusions can be drawn:

(1) The combustion of CH_4 in a NG-diesel dual fuel engine at low loads was dominated by the combustion of the pilot fuel, the relative volumetric ratio of the pilot fuel vapor over the total combustion chamber volume, the movement of the hot

combustion products towards the unburned mixture, and the mixing of the hot combustion products with the unburned CH₄-air mixture.

(2) The spray plume of the pilot fuel injected into the cylinder produced a high velocity field of the bulk gas under the guidance of the piston bowl shape, which helped the mixing of the hot combustion products with the unburned CH₄ and contributes most to CH₄ consumption during the combustion process. The main combustion process consumed 43% to 53% of the CH₄.

(3) The post-combustion oxidation of CH₄ occurred in the interface between the hot combustion products and the unburned pre-mixed mixture. The mixing between the hot combustion products and the cool CH₄-air mixture increased the temperature of CH₄ to that needed for its oxidation. The post-combustion process consumed 17% to 29% of the CH₄.

(4) The unburned CH₄ observed at EVO was located mainly at the center of the cylinder. The portion of CH₄ present at the boundary layer near the cylinder liner was relatively small. The total CH₄ left unburned at EVO was 27 to 35% of the intake CH₄.

(5) The optimization of dual fuel engine design, operation and fuel injection strategies aiming to minimize CH₄ emissions should focus on those capable of increasing the relative volume of the pilot fuel vapor or its combustion products, increasing the chance for unburned CH₄-air mixture to mix with hot combustion products early in the expansion process when the temperature of the combustion products is still high.

The model validated in this research will be applied to develop the fuel injection strategies aiming to minimize the emissions of CH₄. The design of the fuel injection system and combustion chamber geometry can also be optimized using this CFD platform. The optimization of fuel injection strategies in reducing CH₄ emissions will be reported in Chapter 9.

Chapter 6 NO₂ Formation Mechanism in Dual Fuel Engine (QHCV analysis)

This chapter numerically investigated the NO₂ formation pathway in a NG-diesel dual fuel engine. The objective of this chapter is to investigate the in-cylinder distribution and formation mechanism of NO₂ in a NG-diesel dual fuel engine. The simulation is conducted using engine I as platform.

6.1 NO₂ distribution during post combustion stage

Figure 6.1 shows the simulated variation of the peak cylinder temperature, HRR, and the total mass of n-heptane, CH₄, HO₂, OH, NO and NO₂ with changes in CA. The different combustion stages representing specific combustion features as listed in Table 6.1, is marked in Figure 6.1. Notable NO is observed in the 4th combustion stage associated with the late diffusion combustion that occurred within the area featured with local ER over 1 (rich mixture) or around 1 (stoichiometric or even lean mixture) and the 5th stage when hot combustion products are pushed toward the CH₄-air mixture by the driving force produced by the injection spray of the high-pressure pilot fuel and piston movement. The contribution of the 4th and 5th combustion stages to the peak NO observed is 25% and 75%, respectively. In comparison, notable NO₂ is first observed at the 5th combustion stage when the hot combustion products started to mix with the CH₄-air mixture. The majority of NO₂ is formed during the 6th combustion stage representing the post-combustion process during which a portion of the unburned CH₄ that survived the

main combustion process oxidized to either incomplete combustion products or complete combustion products. The formation of NO_2 in the 6th combustion stage is accompanied by the decreased NO and the gradual oxidation of CH_4 . The decreased NO accompanied by NO_2 formation indicated the conversion from NO to NO_2 . Such a process lasted until the CA when temperature of the bulk gas is too low to initiate the oxidation of CH_4 or the mixing between these two different mixture become negligible. It was reported [56, 73, 74] that the OH and HO_2 radicals might play a crucial role in the conversion from NO and NO_2 in the reaction: $\text{OH} + \text{NO}_2 = \text{HO}_2 + \text{NO}$. As shown in Figure 6.1, most of the NO_2 is produced when the NO is observed to decrease, indicating the possible consumption of NO accompanied by NO_2 production.

Figure 6.1 Variation of heat release rate, peak cylinder temperature, the total mass of n-heptane (NC_7H_{16}), CH_4 , HO_2 , OH , NO and NO_2 with change in CA.

Table 6.1 List of combustion stages shown in Figure 6.1

Comb. stage	Main features
1	Premixed combustion of n-heptane
2	Early stage of diffusion combustion
3	Fast diffusion combustion featuring fast consumption of n-heptane
4	Late diffusion combustion of n-heptane accompanied by the combustion of CH ₄ . Combustion occurs mainly in pilot fuel spray plume featured with ER over or around 1
5	Combustion of CH ₄ -air mixture away from pilot fuel spray plume by mixing with hot combustion products featured with ER<1, the combustion products of n-heptane with CH ₄ but lean mixture
6	Post-combustion oxidation of CH ₄

Figure 6.2 shows the bulk mixture temperature and spatial distribution of NO, NO₂, and CH₄ observed over a wide range of CAs. At 10° CA and 25° CA ATDC representing the 4th and 5th combustion stage, respectively, NO is mainly formed in the hot combustion products of pilot fuel as indicated by the high temperature. In comparison, NO₂ concentration in NO-rich hot combustion products is extremely low. There might be NO₂ formed in the hot combustion products, but it is highly-likely to be later dissociated to NO after the complete combustion of n-heptane. As shown in Figure 6.2, the NO₂ at 25° CA ATDC is found mainly at the interface region between the hot combustion products containing NO and the relatively cold unburned CH₄-air mixture. The hot combustion products and cool unburned CH₄-air mixture containing CH₄ is separated by a NO₂-rich region. The NO₂ containing region is first pushed toward the unburned CH₄-air mixture due to the expansion of combustion products and its mixing with the unburned CH₄

mixture. Late in the expansion stroke, the in-cylinder turbulence and the pushing force generated by the pilot fuel injection and combustion become very weak and the bulk gas movement is driven by downward movement of the piston, which dragged the CH₄-air mixture toward the hot combustion products containing NO as shown at 64.7°CA ATDC. As shown in Figure 6.2, the NO₂ observed at 64.7°CA ATDC is mainly located in the interface between the hot combustion products containing NO and the cold CH₄-air mixtures and the boundary layer near the cylinder liner where the unburnt CH₄ is still available. Thus, it is reasonable to assume that the availability of CH₄, NO and the suitable temperature for the oxidation of CH₄ are the key factors for the conversion from NO to NO₂.

Figure 6.2 Temperature and distribution of NO, NO₂ and CH₄ in cylinder simulated at different CAs. From top to bottom: 10°, 25°, 40°, 65° CA ATDC.

6.2 Analysis of NO₂ analysis using a QHCV model

The reaction path and key species dominating NO₂ formation in a dual fuel engine are examined using a QHCV model. The initial temperature, pressure, and composition of

the mixture are set as the average value of these parameters within the region covering 95% of NO₂ simulated at 64.7°CA ATDC (shown in Figure 6.3) as shown in Table 6.2.

Figure 6.4 shows the variations in mixture temperature and the concentrations of NO and NO₂ with changes in time simulated using the QHCV model. The increase in NO₂ concentration is accompanied by the oxidation of CH₄ and consumption of NO. The period from the top dead center (TDC) to EVO for this engine at 1420 rpm is 0.0178 s. The observed increase in the temperature in 0.0178s is about 5 K, which is due to the oxidation of a small portion of CH₄ which has survived the main combustion process. The time period from peak NO timing to EVO is 0.0141 s. As shown in Figure 6.4, the variations of temperature, the NO₂, NO, CH₄ and HO₂ from 0 to 0.02 s are monotonous. The changes in the reaction time may affect the total percentage of NO converted to NO₂ but not affect the results of the reaction pathway analysis. In this research, the reaction pathway analysis is conducted with the assumed reaction time of 0.0141 s. The reaction rates of the reactions associated with the oxidation of CH₄ and the conversion from NO to NO₂ are analyzed to develop the reaction path and the contribution of each reaction to the formation and consumption of the major species.

Figure 6.3 Bulk gas region containing 95% NO₂, which is selected to develop the input data for QHCV model.

Table 6.2 Average temperature, pressure and species molar fraction in the QHCV model

Parameter	Value
Average Temperature	1061K
Pressure	936932 Pa
Average O ₂ Molar Fraction	0.1098
Average N ₂ Molar Fraction	0.7461
Average CO ₂ Molar Fraction	0.0446
Average H ₂ O Molar Fraction	0.0830
Average CH ₄ Molar Fraction	0.0128
Average NO Molar Fraction	0.000176
Average NO ₂ Molar Fraction	0.000219

Figure 6.4 Variation of temperature profile and NO, NO₂ molar fraction with changes in time simulated using QHCV model.

Figure 6.5 shows the reaction path dominating the production of HO₂ and the conversion from NO to NO₂. Table 6.3 shows the reactions discussed in Figure 6.5. Most of the CH₄ consumed (98%) is consumed through R66: CH₄+OH=CH₃+H₂O. The overall

reaction path for the production of HO_2 can be summarized as $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{HO}_2$, with conversion ratios of 98%, 74%, 90%, and 98%, respectively. Among the three reactions consuming HO_2 , the backward reaction of $\text{OH} + \text{NO}_2 = \text{NO} + \text{HO}_2$ consumes 34% of HO_2 and dominates the conversion from NO to NO_2 .

Figure 6.5 Reaction path analysis of the effect of CH_4 to NO_2 production.

Table 6.3 Reactions discussed in Figure 6.5

R27	$\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}$
R36	$\text{CH}_3\text{O} + \text{CO} = \text{CH}_3 + \text{CO}_2$
R45	$\text{H}_2\text{O}_2(+\text{M}) = \text{OH} + \text{OH}(+\text{M})$
R51	$\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$
R52	$\text{CH}_2\text{O} + \text{OH} = \text{HCO} + \text{H}_2\text{O}$
R54	$\text{HCO} + \text{O}_2 = \text{HO}_2 + \text{CO}$
R56	$\text{CH}_3 + \text{CH}_3\text{O} = \text{CH}_4 + \text{CH}_2\text{O}$
R64	$\text{CH}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH}$
R66	$\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$

6.3 Effect of temperature and CH_4 concentration on NO_2 formation.

The QHCV model is applied to investigate the effect of temperature and CH_4 concentration on the conversion from NO to NO_2 . The initial pressure and the molar fraction of NO and NO_2 is set as the value shown in Table 6.2 for all simulation cases. The ER is varied from 0.0 to 1.0 by changing the initial molar fraction of CH_4 and N_2 in the mixture. The temperature is varied from 800 to 1300 K. $t_{\text{NO}_2,90}$ is defined as the time needed for the conversion of 90% NO to NO_2 . A NO to NO_2 conversion reaction rate factor $\tau = \frac{1}{t_{\text{NO}_2,90}}$ is defined to represent the rate of conversion from NO to NO_2 during the CH_4 oxidation process. τ increases with the increase in the backward reaction rate of the reaction $\text{NO} + \text{HO}_2 = \text{NO}_2 + \text{OH}$. The larger the τ , the shorter the time needed for the conversion of 90% NO to NO_2 , and the faster the conversion from NO to NO_2 through the reaction $\text{NO} + \text{HO}_2 = \text{NO}_2 + \text{OH}$.

Figure 6.6 shows the impact of the initial mixture temperature and ER on the NO to NO₂ conversion reaction rate factor. The conversion of 90% NO to NO₂ cannot be achieved when the temperature of the bulk mixture is lower than 890 K under the initial conditions and the time period 0.0141s described. The conversion of 90% NO to NO₂ could not be reached if the temperature is over 1220 K. The failure to achieve the conversion of 90% NO to NO₂ at high temperature is due to the destruction of NO₂ to NO at high temperature. It should be noted that the impact of ER on the conversion factor is very weak as shown in Figure 6.6. It is evident that the conversion from NO to NO₂ is mainly formed at a medium bulk mixture temperature (900 to 1200 K) which is much lower than that for the formation of thermal NO. This is consistent with the previous observation that NO₂ is mainly formed at the interface between the hot combustion products and low temperature zone during the post-combustion process.

Figure 6.6 Effect of initial temperature and ER on NO to NO₂ conversion factor

Figure 6.7 shows the correlation of the average molar fraction of NO and NO₂ with the average temperature and ER within the region where NO and NO₂ exist, respectively. The conversion factor shown in Figure 6.6 is also presented in Figure 6.7 for reference. The average temperature shown in Figure 6.7 is the average temperature of the zone containing NO and NO₂, respectively. The evolution of the molar fraction of NO and NO₂ is consistent with in-cylinder NO/NO₂ molar fraction shown in Figure 6.1. As discussed in the previous section, the formation of NO is first observed at the rich area as indicated with the average ER over 1, the main features of the 4th or earlier combustion stage. The increased formation of NO is accompanied by a decrease in ER without significantly affecting the average temperature of the NO zone indicating the formation of NO in the hot mixture with NO continuously formed in the leaner mixture. The further increase in the average NO

concentration within the NO containing region is accompanied by a decrease in the average temperature and ER, indicating the mixing of hot combustion products containing NO with CH₄-air mixture present outside pilot fuel spray plume, the possible formation of NO in CH₄-air mixture zone featured with lower combustion temperature, and temperature decrease accompanied by the downward movement of piston. After the observation of the peak NO concentration, the decrease in the average NO is accompanied by the decrease in the average temperature and the ER, indicating the combustion of the lean mixture and mixing of the combustion products with the unburned mixtures. The downward movement of the piston also contributed to the decrease in bulk mixture temperature. As shown in Figure 6.7, the NO₂ is mainly distributed in the region where both the average temperature of the mixture and ER are low, indicating the formation of NO₂ in the area consisting of mainly CH₄, air, and residue gas. This is consistent with the formation of NO₂ in the interface between the hot combustion products and the unburned CH₄-air mixture as shown in Figure 6.2. The majority of the NO₂ is formed in the area where the temperature is below 1200 K with very low ER which represented the pilot-fuel free area with NG (CH₄) as the only fuel. The combustion stages representing the development of combustion is also marked in Figure 6.7, indicating the formation of NO₂ during the post-combustion oxidation process of the unburned CH₄. The latter is critical in providing the HO₂ needed for the conversion from NO to NO₂. It should be noted that there is NO₂ formed in the 1400 K to 1900 K region with HO₂ either provided by the oxidation of n-heptane or CH₄ at the edge of the pilot spray plume. However, the NO₂ formed in the high temperature region is

reduced to NO as shown in Figure 6.7. The NO₂ emitted from NG-diesel dual fuel engine is formed mainly in the interface between the NO-containing combustion products and unburned CH₄-air mixture where the temperature is suitable for the conversion from NO to NO₂ but too low for the destruction of NO₂ to NO.

Figure 6.7 The distribution of NO and NO₂ in ER-T diagram over the combustion period. The number marked in figure represents combustion stage.

6.4 Summary

This research numerically investigated NO₂ formation mechanism in a NG-diesel dual fuel engine using a CONVERGE CFD model. The distribution of NO and NO₂ in cylinder and ER-T diagram of a NG-diesel dual fuel engine was reported for the first time. Based on the data presented in this research, the following conclusions can be drawn:

(1) The NO_2 emitted from NG-diesel dual fuel engine was mainly formed in the interface region between the hot NO-containing combustion products and the cool unburned CH_4 -air mixture during the post-combustion expansion process. The oxidation of the CH_4 provided the HO_2 needed for the conversion from NO to NO_2 . The low NO_2 emissions from diesel engine might be due to lack of HO_2 formed during post-combustion expansion process.

(2) The NO_2 formed during the early combustion process was converted to NO due to the high temperature of the combustion products, and the complete consumption of HO_2 present with NO after the complete oxidation of the local CH_4 and n-heptane. The NO_2 observed at EVO was formed mainly in the post combustion expansion process.

(3) The HO_2 needed for the conversion from NO to NO_2 was formed during the CH_4 oxidation process through the reaction path: $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{HO}_2$. The reaction 54: $\text{HCO} + \text{O}_2 = \text{HO}_2 + \text{CO}$ provided 98% of the HO_2 formed in the particular case examined in this research. The backward reaction of $\text{OH} + \text{NO}_2 = \text{NO} + \text{HO}_2$ consumed 34% of HO_2 for the conversion from NO to NO_2 .

(4) The NO to NO_2 conversion reaction was dominated by the temperature of the mixture consisting of NO, CH_4 , O_2 , etc. In comparison, the impact of ER or concentration of CH_4 on the conversion reaction rate factor was negligible.

(5) The distribution of NO and NO_2 in the ER-T diagram confirmed that the NO_2 emitted from a NG-diesel dual fuel engine was mainly formed and distributed in the

mixture with a relatively low temperature. This ruled out the possibility for the NO_2 formed in the hot combustion zone of the pilot fuel to survive until EVO.

Chapter 7 NO₂ Formation Mechanism in NG-Diesel Dual Fuel Engine (Instantaneous Kinetics Analysis)

According to the species conservation equation during CFD calculation:

$$\frac{\partial \rho Y_{NO_2}}{\partial t} = -\nabla \cdot (\rho Y_{NO_2} \vec{V}) + \nabla \cdot (\rho D \nabla \cdot (Y_{NO_2})) + \rho \dot{\omega}_{NO_2} \quad (7.1)$$

Where ρ is density, ∇ is derivative calculator, Y_{NO_2} is mass fraction of NO₂, $\vec{V}$ is velocity vector, $\dot{\omega}_{NO_2}$ is the net production rate of NO₂ obtained from instantaneous ROP calculation, D is diffusion coefficient.

The three terms in the right-hand side of equation (7.1) represent convection, diffusion, and reaction, respectively. The mathematic nature of QHCV analysis is to integrate the $\dot{\omega}_{NO_2}$ in a NO₂-containing isolated volume during a specific period. However, the application QHCV analysis is limited by situations. Firstly, during the post combustion stage, the effect of convection on NO₂ formation/consumption is low due to the weak turbulence, which leads the NO₂ formation dominated by reaction. Secondly, accordingly to Arrhenius expression, the rate of reaction is significantly affected by local temperature. The NO₂ containing isolated volume applied in the QHCV analysis was characterized by low temperature compare with that in main combustion stage, leading the reduced error occurred during the QHCV analysis. These two reasons made the QHCV method available for NO₂ formation analysis during the post combustion stage.

This chapter numerically investigate the NO₂ formation pathway in a NG-diesel dual fuel engine through analyzing the instantaneous kinetic data. The experimental data of Engine II is applied. The simulation results exported from CFD model established in Chapter 3 are analyzed using the post processing tool developed in Chapter 4. The important reactions discussed in this chapter are shown in Table 7.1.

Table 7.1 Key reactions discussed in this chapter

R1	HO ₂ +NO=NO ₂ +OH	R12	CH ₃ +OH=CH ₂ +H ₂ O
R2	O+NO+M=NO ₂ +M	R13	CH ₂ CO(+M)=CH ₂ +CO (+M)
R3	NO ₂ +O=NO+O ₂	R14	CH ₃ +O=CH ₂ O+H
R4	H+NO ₂ =NO+OH	R15	CH ₂ +O ₂ =CH ₂ O+O
R5	C ₇ H ₁₅ =C ₂ H ₅ +C ₂ H ₄ +C ₃ H ₆	R16	CH ₂ O+OH=H ₂ O+HCO
R6	C ₇ H ₁₅ +O ₂ =C ₇ H ₁₅ O ₂	R17	HCO+M=CO+H+M
R7	C ₂ H ₄ +OH=CH ₂ O+CH ₃	R18	H+O ₂ =O+OH
R8	C ₃ H ₆ =C ₂ H ₃ +CH ₃	R19	CH ₄ +OH=CH ₃ +H ₂ O
R9	C ₃ H ₆ +O=CH ₂ CO+CH ₃ +H	R20	H+O ₂ (+M)=HO ₂ (+M)
R10	C ₂ H ₃ +O ₂ =CH ₂ O+HCO	R21	HCO+O ₂ =CO+HO ₂
R11	CH ₃ +O ₂ =CH ₂ O+OH		

7.1 The NO₂ evolution characteristics during combustion

Figure 7.1 shows the effect of the NG substitution on the variations of the total mass and production rate of NO₂, and HRR with change in CA. The NO₂ mass production rate is the derivative of the total NO₂ mass with respect to CA, i.e. $dm_{NO_2}/d\theta$, where m_{NO_2} is the total mass of NO₂ in cylinder. The significant variation in $dm_{NO_2}/d\theta$ before 10 °CA ATDC suggests the strong competition among reactions

that create/destroy NO_2 during the main combustion stage. The addition of NG is found to significantly reduce the NO_2 formed during the early combustion stage. The NO_2 observed at diesel only operation mode (0NG) is mainly produced during the main combustion process with the peak NO_2 production observed before 10°CA ATDC . The substitution of 25%, 50% and 75% diesel by CH_4 elongated the period of NO_2 production beyond the completion of the main combustion, which continued into the late expansion process and even into the EVO. The peak NO_2 production rate is retarded to around 30, 50, and 100°CA ATDC for the cases of 25NG, 50NG, and 75NG, respectively. It is evident that most of the NO_2 emitted from the NG-diesel dual fuel engine are produced during the post combustion process. This research will first examine the NO_2 formation reaction pathway in a NG-diesel dual fuel engine using the 25NG case as an example. The impact of the increased NG addition on NO_2 formation will be examined and discussed.

In this study, the regions of bulk gas with positive and negative net NO_2 production rates are defined as Region 1 and Region 2, respectively. Figure 7.2 shows the variations of the total NO_2 mass in Region 1 and Region 2 with changes in CA for 0NG and 25NG case, respectively. The total mass of NO_2 in Region 1 is much higher than that in Region 2, indicating that the NO_2 in the region having net NO_2 consumption (Region 2) can be ignored. The NO_2 formation mechanism in NG-diesel dual fuel engines can be explained by analyzing NO_2 production in Region 1 due to relatively much less NO_2 in

Region 2.

Figure 7.1 Effect of diesel substitution by NG on the simulated variation of total NO₂ mass, total NO₂ production, and HRR with change in CA

Figure 7.2 Variation of the total NO₂ mass in Region 1 and Region 2 with change in CA for diesel and 25NG, respectively. Red line: Region1, blue line: Region 2.

For the 25NG case, the NO₂ formation mechanism during the main combustion stage and post combustion expansion process is examined at CA50 (7° CA ATDC) and CA95 (60° CA ATDC), respectively. Therefore, the following discussion includes three sub-sections. In section 7.2, the NO₂ formation mechanism during main combustion stage is studied. In section 7.3, the NO₂ formation mechanism at post combustion stage is examined. In section 7.4, the effect of NG substitution ratio on NO₂ formation at 25NG, 50NG and 75 NG during post combustion expansion process is explored.

7.2 NO₂ formation during the main combustion stage

The NO₂ production is determined by reactions R1 and R2 which involve HO₂ and O, respectively. In this research, the in-cylinder region where the production of NO₂ is dominated by R1 involving HO₂ is defined as the RCR_{NO₂-HO₂} region, while the region where the production of NO₂ is dominated by R2 with O involved is defined as the RCR_{NO₂-O} region. Figure 7.3 shows the distributions of NO, NO₂, CH₄, HO₂, O, temperature, RCR_{NO₂} and NO₂ production rate in the bulk gas as well as the phi-T diagram observed at CA50 noted as 7 °CATDC for the case of 25NG. It is found that NO is mainly distributed within the high temperature region indicating the formation of NO in HTC products of diesel, which is consistent with the NO formation characteristics reported in the literature [74, 75]. In comparison, NO₂ is mainly distributed in the interface area between the hot region containing most NO and relatively cool region containing the unburned NG-air mixture as indicated by the distribution of unburnt CH₄.

Both the $\text{RCR}_{\text{NO}_2\text{-O}}$ and $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ regions feature low local ER, indicating that the formation of NO_2 mainly occurs in lean mixtures located at the edge of diesel spray plume. Such a lean mixture can be either the unburned CH_4 -air mixture featured with low temperature or the mixture of n-heptane, CH_4 and air located in the edge of n-heptane spray plume. The local temperature in the $\text{RCR}_{\text{NO}_2\text{-O}}$ region is over 1600K as shown in phi-T diagram, indicating the formation of NO_2 through R2 in the high temperature region representing the region within the pilot fuel spray plume. In comparison, the temperature of the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region (1000 to 1700 K) is much lower than that of the $\text{RCR}_{\text{NO}_2\text{-O}}$ region. As shown in Figure 7.3, the highest NO_2 molar fraction is observed at the interface between the hot combustion products containing a high concentration of NO and the relatively cool region containing CH_4 -air mixture, which is accompanied by high molar fraction of HO_2 . This indicates that the NO_2 observed at 7 °CA ATDC is mainly formed in the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region.

Figure 7.3 Temperature, RCR_{NO2} distribution in cut-plane and phi-T diagram, CH₄, NO, NO₂, HO₂, and O molar fraction, NO₂ production rate at Region1, CA50, 7 °CA ATDC, 25NG case.

The formation reaction pathway of NO₂ in the RCR_{NO2}-HO₂ and RCR_{NO2}-O region at 7 °CA ATDC is investigated using the ISDP method. As shown in Figure 7.4, the instantaneous species destruction pathway in the RCR_{NO2}-O region and RCR_{NO2}-HO₂ region are significantly different. For the RCR_{NO2}-O region, the heptyl radical consumption is dominated by its destruction via R5 instead of oxygen addition via R6, which is well known for low-temperature combustion. The products of R5, such as C₂H₄, C₂H₅, and C₃H₆, in turn produce the formaldehyde radical (CH₂O) through a complex

destruction pathway, leading to the production of a large amount of H and O radical by reaction route $R16 \rightarrow R17 \rightarrow R18$. The H and O radicals not only take part in NO_2 formation through R2 but also NO_2 consumption reaction through R3 and R4. Meanwhile, the reactions R9, R14 and R15 are involved in O/H radical production/consumption, which may also promote the chain branching reaction in the RCR_{NO_2-O} region. Accordingly, the H and O radicals dominating the formation of NO_2 in the RCR_{NO_2-O} region are produced through reaction pathway: $C_7H_{15} \rightarrow CH_2O \rightarrow HCO \rightarrow H \rightarrow O$. In comparison, the formation of NO_2 in the $RCR_{NO_2-HO_2}$ region is dominated by the HO_2 produced through reaction pathway $CH_4 \rightarrow CH_3 \rightarrow CH_2O \rightarrow HCO \rightarrow HO_2$. The HO_2 present in the $RCR_{NO_2-HO_2}$ region is produced through co-oxidation of methane and n-heptane. The examination of the reaction path way identified HCO as the key species dominating the formation of the key radicals such as H and O in the RCR_{NO_2-O} region, and HO_2 in the $RCR_{NO_2-HO_2}$ region. The HCO produced in the RCR_{NO_2-O} and $RCR_{NO_2-HO_2}$ regions can be theoretically traced back to the dissociation of diesel and CH_4 , respectively.

As shown in Figure 7.4 (b) and Table 7.1, the reactions R11, R20, and R21 in $RCR_{NO_2-HO_2}$ region involves O_2 , which suggests the importance of oxygen for HO_2 production and the conversion from NO to NO_2 . This is consistent with the phi-T distribution of the $RCR_{NO_2-HO_2}$ region shown in Figure 7.3, where the low local ER indicates the availability of O_2 . The reactions marked with red and blue in Figure 7.4 (b) represents production and consumption of OH radical, respectively. The OH produced by

R1 may take part in R16 and R19, which promote the chain branching reaction in the $\text{RCR}_{\text{NO}_2}\text{-HO}_2$ region. The production and consumption of HCO and H radicals prior to the formation of O and HO_2 exist in both $\text{RCR}_{\text{NO}_2}\text{-O}$ region and $\text{RCR}_{\text{NO}_2}\text{-HO}_2$ region. The consumption of HCO in the $\text{RCR}_{\text{NO}_2}\text{-O}$ region is dominated by R17 (99%). In comparison, the HCO production in the $\text{RCR}_{\text{NO}_2}\text{-HO}_2$ region is dominated by R17 (68%) and R21 (31%). The consumption of H is dominated by R18 (65%) in the $\text{RCR}_{\text{NO}_2}\text{-O}$ region and by R20 (69%) in the $\text{RCR}_{\text{NO}_2}\text{-HO}_2$ region, respectively. This suggests that the reaction pathway of NO_2 formation and consumption in the $\text{RCR}_{\text{NO}_2}\text{-O}$ and $\text{RCR}_{\text{NO}_2}\text{-HO}_2$ regions are dominated by the competition among these reactions.

(a) $\text{RCR}_{\text{NO}_2}\text{-O Region}$

(b) $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ Region

Figure 7.4 Contribution of reaction to species destruction for the $\text{RCR}_{\text{NO}_2\text{-O}}$ and $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ regions at 7 °CA ATDC, 25NG case.

Figure 7.5 compares the effect of temperature on the forward RRC of R17 and R21, R18 and R20, respectively. The forward RRC of R17 is lower than that of R21 when the local temperature is below 1625K. However, the RRC of R17 increases significantly with the increasing temperature, especially when the local temperature is over 1625K. The RRC of R18 increases exponentially with temperature and is lower than that of R20 when the local temperature is low (<1100K). This helps to explain the different HCO consumption pathways in the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ and $\text{RCR}_{\text{NO}_2\text{-O}}$ regions shown in Figure 7.4. As shown in the phi-T diagram in Figure 7.3, the temperature of the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region is lower than that of the $\text{RCR}_{\text{NO}_2\text{-O}}$ region. This makes R17 dominates HCO consumption

(99%) in the $\text{RCR}_{\text{NO}_2\text{-O}}$ region featuring with high temperature. The consumption of HCO through R21 in the $\text{RCR}_{\text{NO}_2\text{-O}}$ region is negligible. In comparison, the HCO in $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ is consumed through R17 for the production of H and R21 for the production of the HO_2 radical. In comparison, R18 and R20 dominate the H consumption in the $\text{RCR}_{\text{NO}_2\text{-O}}$ and $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ regions, respectively, due to the significantly high and low RRC. The H produced in $\text{RCR}_{\text{NO}_2\text{-O}}$ through R17 can either convert NO_2 to NO through R4 or produce O through R18 which can either convert NO_2 to NO through R3 or convert NO to NO_2 through R2. The consumption of H produced in $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ produces HO_2 through R20, which promotes the conversion from NO to NO_2 through R1. In summary, the consumption of HCO in the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region produces HO_2 through R17 to R20, and R21, and enhances the conversion from NO to NO_2 through R1. In comparison, the consumption of HCO in the $\text{RCR}_{\text{NO}_2\text{-O}}$ region produces H radical and O radicals, which enhances the conversion from NO_2 to NO through R3 and R4, as well as the conversion from NO to NO_2 through R2.

The local temperature is the key factor dominating the reaction pathway shown in Figure 7.4. The CH_4 concentration in the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region is significantly higher than that in the $\text{RCR}_{\text{NO}_2\text{-O}}$ region, leading to the HO_2 production dominated by $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{HO}_2$. It is also observed in Figure 7.5 that increasing local temperature will increase the O and H production in the $\text{RCR}_{\text{NO}_2\text{-O}}$ region and enhance NO_2 destruction to NO by reaction R3 and R4. Thus, the NO_2 net production rate in the

RCR_{NO2}-O region is dominated by the intense competition among R2, R3 and R4. Therefore, although a significantly high temperature and O radical concentration is observed in RCR_{NO2}-O region, the NO₂ produced by R2 due to high temperature and O radical concentration may be consumed by the reverse reaction of R3 and R4. This explains the higher net NO₂ production rate but a lower NO₂ concentration observed in RCR_{NO2}-O region, as shown in Figure 7.3. However, the low temperature in the RCR_{NO2}-HO₂ region inhibits the production of O and H radicals and the destruction of NO₂ to NO. This explains the formation and high concentration NO₂ at the interface between the NO-containing combustion products and CH₄/air mixture due to the high rate of formation and low destruction rates of NO₂ at low temperature region. As a result, the NO₂ produced in the main combustion stage of a NG-diesel dual fuel engine is mainly formed in the RCR_{NO2}-HO₂ region. In comparison, the NO₂ formed in the hot combustion products during the main combustion stage is subsequently reduced to NO.

Figure 7.5 Effect of temperature on the forward RRC of R17, R21, and R18, R20.

7.3 NO₂ formation in post combustion stage

Figure 7.6 shows the distributions of temperature, RCR_{NO_2} region, NO₂ production rate and mole fractions of CH₄, NO, NO₂ simulated for the 25NG case at CA95 (60 °CA ATDC). Negligible NO₂ can be observed in the high temperature zone representing the combustion products of diesel, indicating the complete destruction of NO₂ formed in the hot combustion production zone during the main combustion stage. It is highly likely that the NO₂ that survived to the EVO is formed in the RCR_{NO_2} -HO₂ region, especially during the post combustion stage. Similar to the NO₂ distribution during the main combustion stage (7°CA ATDC), high NO₂ concentration and NO₂ production is observed at the interface between the cool CH₄/air mixture and the hot combustion products containing

NO. As marked in Figure 7.6, there are three regions ((1)-(3) marked in Figure 7.6) featuring high NO₂ concentrations and high NO₂ production rate. These three regions are all located in the RCR_{NO2}-HO₂ region. Thus, it is evident that the NO₂ produced during the post combustion process is mainly formed in the RCR_{NO2}-HO₂ region. There are insignificant amounts of NO and NO₂ observed in the region featuring low temperature and high CH₄ concentration (marked as (4) in Figure 7.6). Such a region is recognized as a “dead” one which does not participate in active chemical reactions, and does not have a chance to mix with hot combustion products but provides the main source of unburned CH₄ [12, 76].

Figure 7.6 The temperature, RCR_{NO_2} distribution, NO_2 production, CH_4 , NO , NO_2 molar fraction simulated at Region1, 60 °CA ATDC, 25NG case.

Figure 7.7 shows the instantaneous contribution of the main reactions to the destruction of species involved in the $\text{RCR}_{\text{NO}_2}\text{-HO}_2$ region at 60 °CA ATDC. The HO_2 needed for NO conversion to NO_2 is produced by the reaction pathway: $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{HO}_2$, which is similar to that observed in the $\text{RCR}_{\text{NO}_2}\text{-HO}_2$ region at 7 °CA ATDC shown in Figure 7.4 (b). Compared with Figure 7.4 (b), the notable difference observed in Figure 7.7 is the more important contribution of R21 to the consumption of

HCO radical. This is due to the decreased temperature during the expansion process, which may make the RRC of R21 more pronounced.

Figure 7.7 Contribution of reaction to species destruction for the $\text{RCR}_{\text{NO}_2}\text{-HO}_2$ region at 60 °CA ATDC, 25NG case.

Analysis of Figures 7.3 and 7.6 reveals the difference of NO_2 formation nature in dual fuel engine during the main combustion stage and the post combustion expansion stage. As discussed before, the HO_2 radical needed for NO conversion to NO_2 in the $\text{RCR}_{\text{NO}_2}\text{-HO}_2$ region is produced via the reaction pathway: $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{HO}_2$. The unique combustion characteristics of NG-diesel dual fuel engines makes the CH_4 necessary for the production of HO_2 still available after the completion of the main

combustion process [76]. The mixing of the unburned NG-air mixture with hot combustion products increases the temperature of CH_4 and initiates the low temperature oxidation reaction of CH_4 which leads to HO_2 production during the post combustion expansion process. The HO_2 produced enhances the conversion from NO to NO_2 at the interface between the hot NO containing combustion products and cool NG-air mixture. The NO_2 formed in the $\text{RCR}_{\text{NO}_2}\text{-HO}_2$ region during the late main combustion and the post combustion expansion process will survive until EVO and exit the engine as NO_2 emissions. In comparison, for a traditional diesel engine, there is neither premixed CH_4 nor available unburned diesel fuel (n-heptane in this simulation) to produce HO_2 after the completion of the combustion process as the diesel is almost completely burned in the diesel engine. Therefore, the NO_2 emissions from a diesel engine are mainly formed during the main combustion process. This explains the formation of more NO_2 in NG-diesel dual fuel engines than in traditional diesel engines, as shown in Figures 3.4 and 7.1.

7.4 Effect of NG substitution ratio on NO_2 formation

As shown in Figure 3.6, the substitution of diesel by NG significantly increased NO_2 emissions with the maximum NO_2 emission observed at 25NG among the 4 cases examined. Further increasing the substitution ratio from 25% to 75% decreased the emissions of NO_2 . As previously discussed, the NO_2 emissions from NG-diesel dual fuel engines are mainly formed in the $\text{RCR}_{\text{NO}_2}\text{-HO}_2$ region through $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{HO}_2$. This observation is further elaborated by examining the volume of

the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region and the average reaction rate of R1 in this region.

A detailed analysis of the NG substitution effect on diesel spray volumetric ratio, hot combustion products and velocity field was presented in a recent study [76]. In order to understand the effect of NG substitution ratio on NO_2 emission, the findings in the previous study need to be revisited. As presented in reference [76], the diesel was continuously injected when the spray tip reached the piston surface. The hot combustion product bounced back toward the centerline of combustion chamber. This suggests that more momentum of the hot combustion products can be made available when more diesel is injected. As a result, the velocity field of the hot NO-containing regions becomes stronger and its volume becomes larger when more diesel fuel is injected.

With the engine speed and load of the four computational cases kept as constant, increasing the NG substitution ratio decreases the mass of diesel injected in each cycle as shown in Table 3.4. The decreased mass of diesel injected may reduce the volume of the diesel spray plume and combustion products of diesel. This may decrease the NO produced within the diesel spray during the main combustion process, and the volume of interface between the hot combustion products and the cool unburned NG-air mixture, and the reaction rates of chemical reactions occurring within this region. This is supported by examining the volume of the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region and comparing the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ distribution observed at different NG substitution ratios. Figure 7.8 and Figure 7.9 shows the distributions of temperature, RCR_{NO_2} region, NO_2 production rate and molar fractions

of CH₄, NO, NO₂ simulated for the 50NG and 75NG case at 60 °CA ATDC. Several common features can be observed by comparing those parameters shown in Figures 7.8 and 7.9 with that in Figure 7.6. Firstly, both the highest NO₂ mole concentration and production rate is observed at RCR_{NO2}-HO₂ region located at the interface between hot NO-containing combustion products and the cool CH₄/air mixture. Secondly, nearly zero NO₂ is produced in regions featuring high temperature representing the combustion products of diesel fuel and NG without diesel spray plume, and regions at relatively low temperature representing the unburned CH₄-air mixture without involving combustion or mixing with combustion products. The volume of the NO₂ containing region, NO₂ mole fraction, as well as NO₂ production rate is found to decrease monotonically with the increasing NG substitution ratio.

Figure 7.8 The temperature, RCR_{NO_2} distribution, NO_2 production rate, CH_4 , NO, NO_2 molar fraction simulated at Region1, 60 °CA ATDC, 50NG case.

Figure 7.9 The temperature, RCR_{NO_2} distribution, NO_2 production rate, CH_4 , NO, NO_2 molar fraction simulated at Region1, 60 °CA ATDC, 75NG case.

Moreover, as shown in Figure 7.10, increasing the substitution ratio from 25NG to 50NG slightly decreased the total volume of the $RCR_{NO_2-HO_2}$ region until about 100 °CA ATDC. The slightly higher $RCR_{NO_2-HO_2}$ region volume is only observed during the late expansion process. However, increasing the substitution ratio from 25NG to 50NG significantly decreased the reaction rate of R1. Therefore, the decreased NO_2 emissions observed at 50NG when compared with 25NG are due to the decreased reaction rate of R1.

Further increasing NG substitution ratio to 75NG further decreased the volume of the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region, R1 reaction rate, and NO_2 formed in the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region. Increasing the substitution ratio decreases the mass of diesel injected into the cylinder, the size of diesel spray plume, and the volume of hot combustion products as the mass of the diesel injected is significantly decreased. At same time, the increased CH_4 concentration at 75NG helps to burn more NG-air mixture presented outside of the diesel spray than that at the lower substitution ratio and decreased the volume of unburned NG-air mixture observed during the late combustion stage and post combustion expansion process. This is due to the burning of more NG-air mixture at higher substitution ratio benefiting from the higher concentration of NG. This is supported by the portion of the unburned CH_4 -air mixture shown in Figure 7.9 compared to 25NG and 50NG cases shown in Figures 7.6 and 7.8, respectively. This explains the variation of the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region observed at 75NG as it is directly associated with the volumes of the hot combustion products and the cool CH_4 -air mixture. Additionally, the variation of the overall reaction rate is not only affected by the volume of the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region but also by the local temperature, concentration of CH_4 , and how the hot NO containing combustion products mix with the cool NG-air mixture. Furthermore, according to the Arrhenius expression, the reaction rate is affected by local temperature. Thus, the factors that affect the local temperature, such as the heat release process and changes in thermal capacity (specific heat), also affect the reaction rate of R1 in the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region. However, the volume of $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region monotonically decreased with the increasing NG substitution ratio.

Figure 7.10 The volume of the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region and average reaction rate of R1 in the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region.

The formation of NO_2 in NG-diesel dual fuel engines is affected by many factors. Among these, the presence of the unburned CH_4 especially after the completion of combustion or other species having the potential to produce HO_2 and NO-containing combustion products, the mixing between the two mixtures during and after the main combustion process, and production of HO_2 during the oxidation process of CH_4 and its reaction with NO previously formed in the hot combustion products are the key factors dominating the formation of NO_2 in NG-diesel dual fuel engines. The control of the formation of NO_2 should focus on the approaches either to minimize or maximize the availability of HO_2 and its reaction with NO when mixed with hot combustion products.

7.5 Effect of NO_x mechanism on NO₂ formation

The previous sections presented a detailed discussion regarding NO₂ formation mechanism in NG-diesel dual fuel engine during the post combustion stage. It is noted that the NO_x kinetics mechanism coupled to PRF mechanism is a reduced 12 steps mechanism. To ensure the robust of these findings, an artificial simulation case is established. The simulation case is based on the 25NG case, all the initial parameters are kept constant except the kinetics mechanism coupled to the CFD model is changed. The new kinetics mechanism coupled is obtained by merging a detailed GRI NO_x mechanism [67] and the reduced PRF mechanism [66]. The detail mechanism containing radicals such NH, HNO, which can be found in Appendix V. The artificial case is referred as A-25NG in the following study.

Figure 7.11 shows the comparison of simulated NO and NO₂ mass with change in crank angle in 25NG case and A-25NG case. Although both the simulated NO and NO₂ in A-25NG case are under predicted compared with 25NG case, the simulated NO and NO₂ in A-25NG case are found to decrease and monotonically after 30 °CA ATDC. This suggest the conversion of NO to NO₂ during the post combustion stage, which is consistent with the observation reported in Figures 6.1 and 7.1.

Figure 7.11 simulated NO and NO₂ mass with change in crank angle in 25NG case and A-25NG case.

Figure 7.12 shows the distributions of temperature, RCR_{NO_2} region, NO₂ production rate and mole fractions of CH₄, NO, NO₂ simulated for the A-25NG case at 60 °CA ATDC. Similar with that reported in Figure 7.6, the NO₂ is also observed at the interface between hot NO and cool unburned methane. The NO₂ formation is produced by two reactions: R1 and R2. The region featuring with RCR_{NO_2} -R1 contains most of the in-cylinder NO₂, which also similar with that reported in the previous sections.

Figure 7.12 The temperature, RCR_{NO2} distribution, NO₂ production, CH₄, NO, NO₂ molar fraction simulated at Region1, 60 °CA ATDC, A-25NG case. Detail NO_x mechanism.

Figure 7.13 shows the ISDP in RCR_{NO2}-HO₂ region shown in Figure 7.12, the NO₂ formation reaction pathway in RCR_{NO2}-HO₂ for A-25NG case is approximately the same with 25NG case as reported in Figure 7.7, i.e. the HO₂ required for the conversion of NO to NO₂ is produced by CH₄ oxidation through pathway: CH₄→CH₃→CH₂O→HCO→HO₂. Therefore, the reduced 12-steps NO_x mechanism is able to simulate NO₂ formation mechanism in NG-diesel dual fuel engine.

Figure 7.13 Contribution of reaction to species destruction for the $\text{RCR}_{\text{NO}_2}\text{-HO}_2$ region at 60 °CA ATDC, 25NG case.

7.6 Comparison between QHCV and instantaneous kinetics analysis

By comparing the analysis regarding NO_2 formation mechanism in NG-diesel dual fuel engines, the instantaneous kinetics analysis conducted this Chapter achieved approximately the same results as those in Chapter 6, which used QHCV analysis. However, the instantaneous kinetics analysis performed in this Chapter discussed the NO_2 formation mechanism not only in the post combustion stage, but also the in main combustion stage. The reaction pathways achieved by ISDP method indicate the instantaneous $\dot{\omega}_{\text{NO}_2}$ in a RCR_{NO_2} region. This indicates that the instantaneous kinetics

analysis has great advantage in CFD analysis, it provides more accurate and comprehensive results.

7.6 Summary

This chapter investigated the NO₂ formation reaction pathway in a NG-diesel dual fuel engine operated at low loads. The reactions dominating NO₂ formation were revealed by examining the instantaneous ROP of key species calculated using the in-house post processing tools with the known temperature, pressure, and concentration of key species simulated using CFD. The formation reaction pathways of key species such as O and HO₂ dominating NO₂ formation were derived. The impacts of temperature on the RRC of key reactions dominating the chemical reactions in the RCR_{NO2}-O and RCR_{NO2}-HO₂ regions were investigated. Conclusions may only be true at the operating conditions investigated and for the engine hardware and simulation software used. Based on the data presented in this research, these conclusions can be drawn:

(1) The NO₂ in a NG-diesel dual fuel engine can be formed in the RCR_{NO2}-O and RCR_{NO2}-HO₂ regions. The RCR_{NO2}-O region represents the formation of NO₂ within the high-temperature combustion products during the main combustion stage of the diesel fuel. The RCR_{NO2}-HO₂ region represents the interface between the hot NO-containing combustion products and the cool CH₄-containing unburned CH₄-air mixture. The increased NO₂ emissions from dual fuel engines are mainly formed in the RCR_{NO2}-HO₂

region.

(2) The HO₂ radical required for NO-NO₂ conversion in the RCR_{NO₂}-HO₂ region is produced by the reaction pathway: CH₄→CH₃→CH₂O→HCO→HO₂. The presence of the RCR_{NO₂}-HO₂ region contributes to the significantly increased NO₂ emissions from a NG-diesel dual fuel engine compared to a traditional diesel engine. The unburned CH₄/air that survives the main combustion stage provides the CH₄ source for production of HO₂ leading to the formation of more NO₂ in NG-diesel dual fuel engines than traditional diesel engines.

(3) The O radical required for NO-NO₂ conversion in the RCR_{NO₂}-O region is produced by the reaction pathway: HCO→H→O, through reaction R17 and R18 with HCO produced during the oxidation process of n-Heptane noted as C₇H₁₅→CH₂O→HCO→H→O→NO₂. The examination of the RRC reveals that the key factor causing R17 and R18 to dominate HCO and H radical consumption is the high temperature. Therefore, the RCR_{NO₂}-O region is featured with high temperature and the presence of rich O. Meanwhile, the high temperature can promote the destruction of NO₂ to NO by R3 and R4. As a result, the NO₂ concentration in the RCR_{NO₂}-O region is lower than that in the RCR_{NO₂}-HO₂ region. In addition, the NO₂ eventually emitted from dual fuel engines is mainly formed in the RCR_{NO₂}-HO₂ region.

(4) The NO₂ emissions from a NG-diesel dual fuel engine is determined by the total volume of RCR_{NO₂}-HO₂ region and R1 reaction rate in the RCR_{NO₂}-HO₂ region.

Compared with the 25NG case, the 50NG case has comparable $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region volume but significantly lower R1 reaction rate due to the combined effect of various factors such as local temperature, CH_4 concentration, and interaction between hot NO-containing combustion products and cool CH_4 /air mixture. The volume and R1 reaction rate of the $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region observed in the 50NG and 75NG cases are both lower than the 25NG case.

(5) An artificial case: A-25NG is established to investigate the performance of detail NO_x kinetics mechanism in NO₂ formation mechanism analysis in NG-diesel dual fuel engine combustion. The simulation results obtained using A-25NG case is approximately the same compared with the 25NG case. The reduced 12-steps NO_x mechanism is able to simulate NO₂ formation mechanism in NG-diesel dual fuel engine.

Chapter 8 CO Formation Mechanism of NG-Diesel Dual Fuel Engine

To extend the instantaneous kinetics analysis regarding NG-diesel dual fuel engine combustion, this chapter numerically investigate the CO formation pathway in a NG-diesel dual fuel engine using Engine II as a platform. The important reactions discussed in this chapter are shown in Table 8.1.

Table 8.1 Key reactions discussed in this chapter

R1	$\text{HCO} + \text{M} = \text{CO} + \text{H} + \text{M}$	R9	$\text{H}_2\text{O}_2(+\text{M}) = 2\text{OH}(+\text{M})$
R2	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	R10	$\text{CH}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH}$
R3	$\text{HCO} + \text{OH} = \text{CO} + \text{H}_2\text{O}$	R11	$\text{CH}_3 + \text{O}_2 + \text{M} = \text{CH}_3\text{O}_2 + \text{M}$
R4	$\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$	R12	$\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$
R5	$\text{O} + \text{OH} = \text{H} + \text{O}_2$	R13	$2\text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$
R6	$\text{H} + \text{O}_2(+\text{M}) = \text{HO}_2(+\text{M})$	R14	$\text{CH}_2\text{O} + \text{OH} = \text{H}_2\text{O} + \text{HCO}$
R7	$2\text{OH} = \text{H}_2\text{O} + \text{O}$	R15	$\text{H} + \text{O}_2 = \text{O} + \text{OH}$
R8	$\text{H} + \text{HO}_2 = 2\text{OH}$		

8.1 The CO distribution characteristics at EVO timing

Figure 8.1 shows the effect of NG substitution ratio on the variations of the total CO mass, CO production rate, and HRR with change in CA. The production rate of CO is the derivative of total CO mass to CA, i.e. $dm_{\text{CO}}/d\theta$, where m_{CO} is the total mass of CO in the cylinder. The peak CO mass is observed at about 10 °CA *ATDC* which is slightly later than the CA at which the peak HRR is observed. Increasing the addition of NG decreases the simulated peak CO mass. This is due to the reduced mass of pilot diesel

injected into the cylinder with the addition of NG (Table 3.4). As expected, most of the CO formed during the main combustion process is later oxidized to CO₂ during the late diffusion combustion and early post-combustion expansion process. The total CO mass starts to decrease after 10 °CA *ATDC*, which is supported by the negative CO production rate shown in Figure 8.1. However, the addition of NG inhibits the consumption (increases the production rate) of CO after the main combustion stage. As a result, the total CO mass simulated for the 0NG case becomes lower than that of the 25NG, 50NG, 75NG cases after 50, 60, and 80 °CA *ATDC*, respectively.

Figure 8.1 Effect of diesel substitution by NG on the simulated variation of total CO mass, total CO production rate, and in-cylinder HRR with change in CA

In order to analyze the fundamental difference in CO formation and destruction between NG-diesel dual fuel combustion mode and diesel-only combustion mode, the formation and consumption for the CO at 0NG and 25NG cases are examined numerically. Figure 8.2 compares the distribution of the CO molar fraction in the cylinder observed at EVO for 0NG and 25NG cases, respectively. The addition of NG significantly increases the volume of the CO-containing mixture. The high CO concentration region of both 0NG and 25NG are located at the top of the combustion chamber around the cylinder head. Such a high CO concentration region is referred to as Region-H. In comparison, the in-cylinder region where the CO concentration is low is referred to as Region-L.

Figure 8.2 In-cylinder CO mole fraction distributions of 0NG and 25NG cases at EVO. The cut-plane cross of Region-H is shown in the up right of each Figure

Figure 8.3 shows the mass of CO in Region-H and Region-L for 0 NG and 25NG at EVO. The mass of CO in Region-L is comparable with that in Region-H for the 0NG case. However, there is more CO mass in Region-L than that in Region-H for the 25NG case. The addition of NG significantly increases the mass of CO in both Region-H and Region-L. The total mass of CO in Region-L for 25NG is much higher than 0NG.

Figure 8.3 Total mass of CO in Region-H and Region-L shown in Fig. 3 at EVO

8.2 CO formation/consumption mechanism in Region-H

The simulation results shown in Figures 8.1-8.3 suggest that the formation and consumption mechanisms of CO in diesel-only and NG-diesel dual fuel engine operation during the post combustion stage are different. It can be observed in Figure 8.1 that the second zero overall CO consumption rate of the 75NG case is observed at around 50 °CA ATDC, indicating that the balance between the total CO produced and consumed, while those of other cases are observed at CA later than 50 °CA ATDC. Meanwhile, the 50 °CA ATDC represents 94.4% and 93.8% total heat release, for the 0NG and 25NG cases, respectively. Thus, it is reasonable to select the 50 °CA ATDC as a representative timing to

investigate the CO formation and consumption mechanism after the main combustion process (CA10 to CA90) for both diesel-only and NG-diesel dual fuel combustion mode. The CO formation and consumption pathways in Region-H at 50 °CA ATDC are first investigated and discussed for the 0NG and 25NG cases, respectively, followed by the CO formation and consumption mechanisms in Region-L. These will help to explain the difference in CO formation and consumption mechanisms between diesel combustion mode and NG-diesel dual fuel combustion mode.

Figure 8.4 shows the simulated temperature, mole concentrations of CO and O₂, the distribution of $R_{CR_{CO}}/R_{DR_{CO}}$, and CO creation/destruction rate in Region-H at 50 °CA ATDC for 0NG case. The arrows shown in the temperature Figure represent the in-cylinder velocity fields. The CO inside the red-circle is Region-H. As shown in $R_{CR_{CO}}$ and $R_{DR_{CO}}$ distribution Figure, the formation and consumption of CO can be divided into three regions: (1) $R_{CR_{CO}}-R1$ region where the net CO production rate is positive and the CO formation is dominated by R1; (2) $R_{DR_{CO}}-R1$ region where the net CO production rate is negative and CO destruction is dominated by R1; (3) $R_{DR_{CO}}-R2$ region where the net CO production rate is negative and CO destruction is dominated by R2. The $R_{CR_{CO}}-R1$ region is located between the $R_{DR_{CO}}-R1$ and $R_{DR_{CO}}-R2$ regions, which suggests that CO in Region-H is first formed in $R_{CR_{CO}}-R1$ through R1 and is oxidized to CO₂ in $R_{DR_{CO}}-R2$.

Figure 8.4 Simulated temperature, mole concentrations (unit: kmol/m³) of CO, O₂, RCR_{CO}/RDR_{CO} distribution, and CO creation/destruction rate (unit: kmol/m³/CA) at 50 °CA ATDC for 0NG case, Region-H

Figure 8.5 shows the scatter plots of temperature, net CO production rate, and mole concentrations of CO, H, O₂, and OH as a function of mixture fraction. The peak temperature is observed in the mixture fraction range from 0.06 to 0.07. This is referred to as critical mixture fraction range noted as mf_{cr} , which corresponds to the interface between the RCR_{CO}-R1 and RDR_{CO}-R1 region, as shown in Figure 8.4. The mf_{cr} represents the transition zone separating the regions dominated by the forward and reverse reactions of R1. As shown in Figures 8.4 and 8.5, the net CO creation/destruction rate at the

mf_{cr} is significantly higher than others. In comparison, the CO destruction rate in other locations including the RDR_{CO}-R2 region is negligible especially at a low mixture fraction (<0.04). The highest H and OH concentration is also observed at the mf_{cr} . Therefore, the CO formation/consumption in Region-H during the post-combustion expansion process represented by 50 °CA *ATDC* is dominated by the intense competition between the forward and reverse reaction of R1. For mixtures with a mixture fraction less than 0.04, the CO mole fraction is close to zero, while the O₂ mole fraction gradually increases due to less involvement of the combustion products of diesel fuel. With an increasing mixture fraction over the mf_{cr} , a gradually decreasing temperature, near zero O₂, and a significantly high CO concentration is observed. This is due to the more incomplete combustion caused by the lack in O₂.

As shown in Figure 8.4, the bulk gas movement drives the hot bulk gas with high CO concentration toward the fresh NG-air mixture characterized by a high O₂ concentration and low temperature. This leads to the CO consumption by R2 (RDR_{CO}-R2 region) benefiting from the mixing between the hot CO-containing combustion products and the cool O₂-containing fresh air during the post-combustion expansion process. To further examine the CO consumption process, the contributions of key reactions to CO production and consumption in RCR_{CO}-R1 and RDR_{CO}-R2 region are examined using the ISDP method.

Figure 8.5 Scatter plot of mixture fraction versus temperature, net CO production rate (unit: $\text{kmol/m}^3/\text{CA}$) and mole concentrations (unit: kmol/m^3) of CO, OH, H, and O_2 in Region-H. 50 °CA ATDC, 0NG case

Figure 8.6 shows the ISDP in $\text{RCR}_{\text{CO-R1}}$ and $\text{RDR}_{\text{CO-R2}}$ regions within Region-H simulated at 50 °CA ATDC for the 0NG case. As expected, the CO formation in $\text{RCR}_{\text{CO-R1}}$ region is dominated by R1. In comparison, the formation of CO in $\text{RDR}_{\text{CO-R2}}$ region is dominated by R3 while its destruction is dominated by R2. This can be verified by examining the RRC of R1 and R3. As shown in Figure 8.7, the RRC of R1 is lower than that of R3 when the temperature is lower than 1710K, but exponentially increases with temperature. It is evident that the temperature of the mixture has significant effect on CO destruction. Therefore, the competition between R1 and R3 for HCO consumption is controlled by the mixture's temperature. As shown in Figures 8.4 and 8.5, the temperature

of the $\text{RDR}_{\text{CO-R2}}$ region is lower than that of the $\text{RCR}_{\text{CO-R1}}$ region. Meanwhile, the O_2 concentration in the $\text{RDR}_{\text{CO-R2}}$ region is higher than that in the $\text{RCR}_{\text{CO-R1}}$ region. The CO destruction in both $\text{RCR}_{\text{CO-R1}}$ and $\text{RDR}_{\text{CO-R2}}$ regions is dominated by R2, which is consistent with that reported in the literature [20]. It is also observed that the destruction of the H atom is dominated by R5, followed with notable contribution of R6 in both the $\text{RCR}_{\text{CO-R1}}$ and $\text{RDR}_{\text{CO-R2}}$ regions. Both the R5 and R6 involve O_2 , indicating the importance O_2 for CO consumption during the post combustion stage. The destruction of the O radical produced through R5 is dominated by R7 for the production of OH. The HO_2 produced by R6 is consumed by R8 (49% and 40%, respectively, in $\text{RDR}_{\text{CO-R2}}$ and $\text{RCR}_{\text{CO-R1}}$ regions) to produce OH. The OH radicals produced by R5, R7 and R8 further promote the CO consumption by R2. Such a reaction loop accelerates the consumption of CO as shown in Figure 8.6. Therefore, the analysis of Figures 8.4 to 8.7 reveals that the HCO radical acts like a reservoir that stores CO in a H-rich $\text{RDR}_{\text{CO-R1}}$ region and then decomposes to CO and H radicals as it continues to mix with an O_2 containing mixture, such as air, and further oxidized to CO_2 .

Figure 8.6 Instantaneously reaction path flux for RCR_{co}-R1 and RDR_{co}-R2 region at 50 °CA ATDC for the 0NG case

Figure 8.7 The variation of RRC of R1 and R3 with changes in temperature

Figure 8.8 summarizes the CO production and consumption pathway in Region-H at 50 °CA ATDC simulated for the 0NG case. The CO present in RDR_{co}-R1 is first converted to HCO through R1, which is later destructed to CO through reaction R1 in the RCR_{co}-R1 region. The OH radical produced by R5, R7 and R8 promotes the CO

consumption through R2. Such a CO consumption loop continues to occur until the EVO timing, but gradually becomes weaker during the late expansion process due to the decreasing temperature. The CO formed during the main combustion process is gradually consumed and converted to CO₂ when the CO-containing mixture mixes with O₂-rich mixtures such as air during the post-combustion expansion process. There is almost no new CO formed in Region-H during the post-combustion expansion process in 0NG case, which explains the relatively low CO emissions from diesel engines. This observation also explains the numerical results of Kook et al. [77], who noted that optimized swirl ratio could significantly reduce CO emissions from a diesel engine. Increasing swirl ratio can improve the mixing between air and the high-temperature incomplete combustion products containing CO which produces more OH and enhances CO consumption during the main combustion stage and post-combustion expansion process.

Figure 8.8 CO production and consumption pathway in diesel engine at 50 °CA ATDC for the 0NG case

Figure 8.9 shows the simulated temperature, mole concentrations of CO, O₂, RCR_{CO}/RDR_{CO} distribution, and CO creation/destruction rate within Region-H at

50 °CA *ATDC* for 25NG case. Figure 8.10 shows the scatter plots of temperature, net CO production rate, and mole concentrations of CO, H, O₂, and OH as a function of mixture fraction within Region-H at 50 °CA *ATDC* for 25NG case. Several common features are observed by comparing Figures 8.4 and 8.9, and Figures 8.5 and 8.10: (1) The CO is converted to the HCO radical in the RDR_{CO}-R1 region by reaction R1; (2) The HCO is then destructed to CO in RCR_{CO}-R1 region which is oxidized to CO₂ by R2 in RDR_{CO}-R2 region; (3) There exists a critical mixture fraction mf_{cr} between 0.06 and 0.07 where the peak temperature, the highest CO creation and destruction rates, and the highest H and OH concentration are observed; (3) the CO is mainly observed in RDR_{CO}-R1 region, and the H radical is mainly formed in RCR_{CO}-R1 and RDR_{CO}-R1 region.

The addition of NG significantly weakens the chemical reactivity within n-heptane spray by reducing the concentration, production rate, and the consumption rates of reactive radicals such as H and OH [78]. The diesel fuel injected is decreased while introducing NG into intake air as the load and speed were kept as constant. The volume of Region-H at 50 °CA *ATDC* observed at 0NG is higher than that observed at 25NG (Figures 8.4 and 8.9), leading to less computational cells in Figure 8.10 (25NG case) than that in Figure 8.5 (0NG case). The addition of NG may enhance the incomplete combustion of diesel fuel by increasing thermal capacity and reducing O₂ concentration. The NG addition also weakens the reactivity during the post combustion stage in NG-diesel dual fuel combustion. As shown in Figures 8.5 and 8.10, the peak temperature for 25NG case is 2137 K, which is

lower than the peak temperature of 2183 K observed in the 0NG case. Meanwhile, the peak concentration of the H and OH radicals, as well as the production and consumption of CO observed in the 25NG case are also lower than the 0NG case. This inhibits the CO reaction loop shown in Figure 8.7 for 25NG case, causing the weakened CO consumption by R2 in the RDR_{CO} -R2 region. As a result, the CO formed in Region-H in the 25NG case is higher than in the 0NG case, as shown in Figure 8.3 although the total volume Region-H at 25NG case is less than 0NG case.

Figure 8.9 the simulated temperature, mole concentrations (unit: kmol/m³) of CO, O₂, RCR_{CO}/RDR_{CO} distribution, and CO creation/destruction rate (unit: kmol/m³/CA) at 50 °CA ATDC for 25NG dual fuel combustion case, Region-H

Figure 8.10 Scatter plot of mixture fraction versus temperature, net CO production rate (unit: $\text{kmol}/\text{m}^3/\text{CA}$) and mole concentrations (unit: kmol/m^3) of CO, OH, H, and O_2 in Region-H. 50 °CA ATDC, 25NG case

8.3 CO formation/consumption mechanism in Region-L

Figures 8.11 and 8.12 show the distribution of temperature, mixture fraction, mole fractions of CO, OH, and CH_4 , RXR, RCR_{CO}, and RDR_{CO}, the positive CO creation rate, and the positive CO destruction rate (i.e. negative CO creation rate) in Region-L simulated at 50° CA ATDC for 0NG and 25NG, respectively. There are some common features for the 0NG and 25NG cases regarding the CO-containing region. For example, the CO formation and consumption are dominated by R4 and R2, respectively. However, the chemical reactions in Region-L for the 0NG and 25NG cases are significantly different. These differences include: (1) the volume and average concentration of the CO-containing

region observed at 0NG case are significantly lower than those for the 25NG case; (2) for the 0NG case, most of the CO-containing region is characterized by negative net CO production rate (destruction). However, most of the CO-containing region in Region-L of the 25NG case is characterized by positive net CO production rate (creation); (3) for the 0NG case, the high CO concentration is located at the same region as the high concentration CH₄ (marked as “1” in Figure 8.11), which indicates that both the CO and CH₄ is produced by slow oxidation of diesel fuel. In comparison, the high concentration CO in Region L at 25NG case is located at the region with mild CH₄ concentration (marked as “1” in Figure 8.12), indicating that the CO in the dual fuel combustion mode may have a strong relationship with CH₄ oxidation; (4) the mixture fraction at a high CO concentration region of 0NG is obviously lower than that of 25NG. Accordingly, the temperature at high CO concentration region of 0NG (below 800K) is obviously lower than that of 25NG (about 1000K). This suggests that more chemical heat is released during the oxidation process of 25NG than that of 0NG. Most diesel fuel has been consumed at 50 °CA ATDC. However, there is still unburned CH₄; (5) the CO consumption region (RDR_{CO}) is much larger than the CO creation region (RCR_{CO}) in the 0NG case while the situation reverses for the 25NG case, suggesting that CO is primarily consumed for the 0NG case but is still created for the 25NG case during the post-combustion process.

Figure 8.11 The distribution of temperature, mixture fraction, mole fraction of CO, OH, and CH₄, RXR and RCR_{CO}/RDR_{CO}, the positive CO creation rate, the positive CO destruction rate (i.e. negative CO creation rate), 50 °CA ATDC, region-L, 0NG case. Unit of reaction rate: kmol/m³/°CA

Figure 8.12 The distribution of temperature, mixture fraction, mole fraction of CO, OH, and CH₄, RXR and RCR_{CO}/RDR_{CO}, the positive CO creation rate, the positive CO destruction rate (i.e. negative CO creation rate), 50 °CA ATDC, region-L, 25NG case. Unit of reaction rate: kmol/m³/°CA

A detailed analysis of the NG substitution effect on hot combustion products and velocity field was presented in a recent study [76]. It was suggested that the diesel spray plume impinged on the piston bowl surface during the diesel fuel injection process. The hot combustion products bounced back toward the centerline of the combustion chamber and remained near the cylinder head, which was recognized as the source of CO in Region-H discussed in the previous section. However, a small portion of diesel fuel injected at the late injection stage remained near the injector tip due to lack of driving force. This small amount of diesel fuel is located at the spray periphery and forms an extremely lean diesel-air mixture. This is consistent with the Region-L featured with a significantly low mixture fraction. The source of CO produced in Region-L can be revealed by comparing the characteristics of key parameters for the 0NG and 25NG cases. The CO formation in Region-L of the diesel combustion mode is dominated by the slow oxidation of an extremely low concentration diesel fuel combustion product located at the center of the cylinder, while the co-oxidation between the low concentration diesel fuel and CH_4 /air mixture dominates the CO formation in the NG-diesel dual fuel combustion mode. This is the primary reason that the CO emissions from NG-diesel dual fuel combustion mode are higher than those from the diesel-only combustion mode. Detailed analysis on how the low concentration diesel fuel and CH_4 /air mixture dominates the CO formation in the NG-diesel dual fuel combustion mode is provided below for the primary reaction (heat release) zones.

The chemical heat release in the CO-containing regions is dominated by three reactions including R6 (RXR-R6), R10 (RXR-R10), and R11 (RXR-R11). In order to understand the impact of the interaction among lean diesel fuel/air, NG/air mixture, and local heat release on CO formation in NG-diesel dual fuel engine, the mean values of some parameters, as well as the ISDP of species in these RXR regions are examined and compared. These parameters include mixture fraction, temperature, mole concentration of CO, CH₃O₂, O₂, CH₄, H, OH, H₂O₂, and CH₃, total species mole concentration, net production rate of CO, and the pvs of R2, R6, R10 and R11, as shown in Figures 8.13 and 8.14.

Figure 8.13 Average values of mixture fraction, temperature, mole concentrations (Unit: kmol/m³) of CO, CH₃O₂, O₂, CH₄, H, OH, H₂O₂, CH₃, and third body species, net production rate (unit: kmol /m³/s) of CO, and pv (unit: kmol /m³/s) of R2, R6, R10 and R11 in RXR-R6, RXR-R10 and RXR-R11 region for 25NG case

Figure 8.14 ISDP in RXR-R11 (a), RXR-R10 (b), and RXR-R6 (c) regions for 25NG case. The reactions marked with blue consume O_2

The RXR-R6, RXR-R10, and RXR-R11 regions are explored by calculating the pvs of reactions R6, R10, and R11 by equation (4). Figure 8.15 shows the effect of temperature on the forward and reverse RRC of R6, R10 and R11. The forward RRCs of R6, R10, and R11 are higher than their reverse RRCs when temperature is below 1400K. However, the difference between forward RRCs and reverse RRCs for these three reactions are different. For R6 and R10, the forward RRCs are over 5 orders of magnitude higher than their reverse RRCs. In comparison, the forward RRC of R11 is about 2 orders of magnitude (100 time) higher than its reverse RRC. Accordingly, the reverse reactions of R6 and R10 are negligible since the average temperatures in the RXR-R6 and RXR-R10 regions are below 1200K. The pv of reactions R6, R10, and R11 can be expressed as:

$$q_6 = k_{f_6} [H][O_2][M] \quad (8.1)$$

$$q_{10} = k_{f_{10}} [CH_3][O_2] \quad (8.2)$$

$$q_{11} = k_{f_{11}} [CH_3][O_2][M] - k_{r_{11}} [CH_3O_2][M] \quad (8.3)$$

where M is the summation of weighted third body concentrations.

As shown in Figure 8.13, the average mixture fraction and temperature monotonically increase from the RXR-R11 region to the RXR-R10 and RXR-R6 regions. The increased mixing of diesel fuel, as indicated by the increased mixture fraction, may enhance the chain branching reaction in diesel/NG/air mixture and increase the local temperature by releasing more chemical energy. Therefore, the consumption of CH_4 and O_2 and the production of chain branching reaction products such as H and OH monotonically increases with increasing mixture fraction. The third body concentration ($[M]$) in the RXR-R11 region is about 0.18 kmol/m^3 (Figure 8.13), but the forward RRC of R11 ($1.13\text{E}7$) is about 6.5 times higher than that of R10 ($1.73\text{E}6$) when the temperature is 841K as marked in Figure 8.15. The q_{11} calculated by equation (8.3) is larger than the q_{10} calculated by equation (8.2). The p_v of R11 is higher than that of R10 as the temperature is low. The chemical reactions in this region is dominated by R11 which makes it the RXR-R11 region.

Figure 8.15 Forward and reverse RRC of R6, R10 and R11 with change in temperature

As shown in Figure 8.13, the average pv of R11 in the RXR-R10 region is negative. Reaction R11 in RXR-R10 occurs toward the reverse direction, which is endothermic. This can be explained by two reasons: (1) the ratio of k_{f11}/k_{r11} is about 30 due to the increased average temperature in the RXR-R10 region (1104K); (2) the average mole concentrations of CH_3 , O_2 , CH_3O_2 radicals are about $6\text{E-}8$, $2\text{E-}2$, $5\text{E-}8 \text{ kmol/m}^3$, respectively. The term $[\text{CH}_3][\text{O}_2]$ is 2.4% of $[\text{CH}_3\text{O}_2]$. Thus, reaction R11 in the RXR-R10 region proceeds toward the reverse direction which produces a large amount of CH_3 radical (Fig. 14). This is further confirmed by examining the ISDP of the RXR-R11 and RXR-R10 regions. As shown in Figure 8.14 (a), the destruction of CH_3 radical in the RXR-R11 region is dominated by R11(94%). In comparison, the contribution of R10 to CH_3 radical destruction in the RXR-R11 region is negligible (5%) but very important in the RXR-R10 region (77%).

As shown in Figures 8.14 (a) and (b), the formation of CO in Region-L of the 25NG

case is dominated by the reaction pathway: $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{CO}$. The weak pv of R10 in the RXR-R11 region inhibits the production of CO by R4 and therefore decreases the production of H_2O_2 radical through R13. In comparison, the pv of R10 is enhanced by the high CH_3 concentration in the RXR-R10 region which enhances the chain branching and produces more HO_2 and CO.

The ISDP in the RXR-R6 region is significantly different from those in the RXR-R10 and RXR-R11 regions. As shown in Figures 8.14, the consumption of HCO radical in the RXR-R11 and RXR-R10 regions are dominated by R4 which consumes 89% and 83% HCO, respectively. In comparison, the HCO in RXR-R6 region is consumed by R4 and R1 which consume 60% and 39% HCO, respectively. This can also be explained by comparing the expression of pv of R1 and R4 calculated by equation 4.1. As shown in Figure 8.16, the forward RRC of R1 ($9.6\text{E}7$) is about 16.6 times less than that of R4 ($1.59\text{E}9$) at 1212K. However, as shown in Figure 8.13, the average mole concentration of O_2 in RXR-R6 region is about 0.0175 kmol/m^3 , which is 14% of the third body species concentration (0.125 kmol/m^3). The first term of pv expression for R1 ($k_{f_1}[\text{HCO}][\text{M}]$) is comparable with that for R4 ($k_{f_4}[\text{HCO}][\text{O}_2]$), leading to the R1 making notable contribution to CO formation in the RXR-R6 region due to the higher third body concentration [M]. On the other side, the temperatures RXR-R10 and RXR-R11 region are lower than that in the RXR-R6 region, which inhibits the forward RRC of R1, leading to negligible contribution of R1 to HCO destruction. The significantly increased H radical

concentration produced by R1 in the RXR-R6 region enhances the reaction rate of R6. This is supported by ISDP shown in Figure 8.14 (c), where R6 consumes 91% of H radical. Meanwhile, Most of the CH_3 radical is consumed in the RXR-R6 region (Figure 8.13), which inhibits the chemical heat release through R10 and R11. As a result, the chemical heat release is dominated by R6, causing the formation of the RXR-R6 region.

Figure 8.16 The RRC of R1 and R4 with variation of temperature

Figure 8.17 shows the variation of the forward RRC of R9 with change in temperature. The RRC of R9 becomes notable at about 1000K and exponentially increases with increasing temperature. The rate of OH production by R9 monotonically increases with increasing temperature and H_2O_2 concentration. The formation and consumption of CO at 50 °CA ATDC in all of these RXR regions in Region-L is dominated by the reaction pathway: $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{CO}$ and reaction R2, respectively. The concentration of diesel fuel and its combustion products that mixes with CH_4 /air are the key parameters that affect the concentration as well as the ISDP of species for the NG-diesel dual fuel combustion mode. The RXR-R10 and RXR-R11 regions are featured

with low temperature and low concentration of diesel fuel combustion products as indicated by the low mixture fraction, close to that of the premixed NG-air mixture. The temperature in these two regions is too low to produce OH radicals which is crucial for the CO oxidation through R2. Accordingly, the CO produced in the RXR-R10 and RXR-R11 regions during the post combustion expansion process can not be further oxidized to CO₂, but survives through the post combustion expansion process. This reveals the reason why the CO concentration in the RXR-R10 and RXR-R11 regions in Region-L is significantly higher at the dual fuel combustion mode than diesel-only mode. The RXR-R10 and RXR-R11 regions in Region-L are the main sources of the CO emissions from the NG-diesel dual fuel engine. Accordingly, the increased CO emitted from NG-diesel dual fuel engine is mainly formed in the NG-air mixture where the mixing of the hot combustion products mixed with unburned methane-air mixture during the post combustion explosion process. The temperature in CO production region is high enough to initiate the oxidation of CO but not sufficient to support the oxidation of CO to CO₂.

Figure 8.17 Variation of the forward RRC of R9 with change in temperature

Figure 8.18 shows the ISDP in the RXR-R6 and RXR-R11 regions for the 0NG case shown in Figure 8.11. Although the destruction pathway for CH_3 radical consumption in RXR-R6 and RXR-R11 regions is different for, i.e. by R10 and R11, respectively, the CO formation pathway in the RXR-R6 and RXR-R11 regions for the 0NG case can also be summarized as: $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{CO}$, which is similar to that for the 25NG case shown in Figure 8.14. It is obvious that the reaction pathway: $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{CO}$ determines the maximum amount of H_2O_2 and CO radical before the possible ignition happens. However, for the 0NG case, the mixture fraction in Region-L is significantly lower than that for the 25NG case, leading to the extremely low CO production. This makes the CO emissions from NG-diesel dual fuel engines significantly higher than that from traditional diesel engines.

Figure 8.18 ISDP for RXR-R6 and RXR-R11 regions for 0NG case shown in Figure 8.12

8.4 Summary

This research numerically investigated the CO formation and consumption pathway in the NG-diesel dual fuel engine using Converge model. The CO-containing region in the cylinder can be categorized into Region-H and Region-L in both the diesel only and the NG-diesel dual fuel combustion modes. The formation and consumption of CO during the post-combustion process were numerically investigated in both diesel and NG-diesel dual fuel engine. All the following statements may only be true at the operating conditions investigated, the engine hardware used, and the fuel chemistry integrated. Based on the simulation results obtained in this research, the following conclusions can be drawn:

- (1) The CO in Region-H was mainly produced by incomplete combustion of

the diesel fuel during the main combustion stage. In comparison, the CO in Region-L of the 25NG case was produced by slow oxidation of lean diesel fuel, and oxidation of NG when mixed with the combustion products of lean diesel-air mixture formed during the main combustion process.

(2) The CO formation/consumption in Region-H of the diesel-only and NG-diesel dual fuel combustion mode was dominated by the intense competition between the forward and reverse reaction $\text{HCO}=\text{H}+\text{CO}$ at the interface between the $\text{RDR}_{\text{CO-R1}}$ region and the $\text{RCR}_{\text{CO-R1}}$ region. The consumption of CO formed in Region-H was dominated by reaction $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$ which is affected by the entrainment of O_2 -containing mixtures into the CO-containing region. The CO produced during the main combustion stage was consumed through $\text{CO}\rightarrow\text{HCO}\rightarrow\text{CO}\rightarrow\text{CO}_2+\text{H}\rightarrow\text{OH}$. The OH radicals enhances the CO consumption during the post-combustion expansion process.

(3) The CO formation/consumption mechanism in Region-H was similar for both diesel engine combustion and NG-diesel dual fuel combustion modes. The addition of NG to intake air weakened the reactivity in region-H by reducing the temperature and concentration of reactivity radicals such as H and OH, leading to the weakened reaction loop in the $\text{RDR}_{\text{CO-R2}}$ region. Therefore, the CO formation or concentration in Region-H for dual fuel mode was higher than that for diesel combustion mode.

(4) The CO formation/consumption mechanism in Region-L for the diesel only mode and dual fuel mode was significantly different. The CO in Region-L of diesel-only

mode was produced by lean diesel-air fuel mixture near the spray periphery. The CO formed was later consumed during the post combustion stage. However, the CO in Region-L of dual fuel mode was produced by co-oxidation of CH₄/air mixture and lean diesel-air mixture and its combustion products, which significantly increase the formation of CO in Region-L of dual fuel engine.

(5) The CO formation/consumption mechanisms and the reactions dominating the heat release in Region-L of the dual fuel mode was significantly affected by the mixing of diesel combustion products with CH₄/air mixture. At lean mixture (RXR-R10/RXR-R11), the net CO production rate was positive (creation) and the CO production was dominated by R2, while the heat release was dominated mainly by R10 and R11. As mixture fraction gets higher (RXR-R6), the net CO production rate was negative (destruction), the CO consumption was dominated by R4, and the heat release was dominated by R6.

(6) The CO in Region-L of the 25NG case was formed by reaction pathway: CH₄→CH₃→CH₂O→HCO→CO and consumed by R2. The CO from the NG-diesel dual fuel combustion mode was mainly formed during the mixing process of the extremely lean diesel fuel and its combustion products with CH₄/air mixture where the local temperature was able to initiate the oxidation of CH₄ to CO, but too low to produce OH radical necessary for the consumption of CO through R2.

Chapter 9 CH₄ Emission Optimization of NG-diesel Dual Fuel Engine

As discussed in Chapter 5, the diesel fuel injection strategies have significantly impact on CH₄ combustion. This chapter explores the potential of CH₄ emission reduction by varying injection strategies such as injection spray angle, injection timing, and multi-pulse pilot fuel injection strategies. The optimization is based on 25NG case that has been validated in Chapter 3 using engine II.

9.1 Effect of spray angle on CH₄ emissions

It has been discussed in Chapter 5 that the driving force caused by high pressure diesel injection spray plays important role in enhancing the mixing of the pilot fuel and the premixed CH₄-air mixture. The distribution of diesel fuel in-cylinder dominated by the injection strategy in turn determines the volume of pilot fuel vapor, and the area of interface between hot combustion products and cool unburned CH₄, which has a strong effect on CH₄ emissions. Therefore, the injection strategy of diesel fuel is an important parameter affecting CH₄ emissions. The emissions of unburned CH₄ from NG-diesel dual fuel engine can be decreased through the optimization of pilot fuel injection strategies.

The objective of this chapter is to explore the potential of minimizing CH₄ emissions by varying injection spray angle and injection timing of pilot fuel injection

under multi-pulse injection condition. The setting of computational case is based on 25NG case that has been validated in Chapter 3 using engine II. Firstly, 80% of total diesel fuel mass injected in 25NG case was applied, the injection pressure, injection timing, and other boundary conditions such as temperature and pressure were kept the same as that in 25NG case. The injection spray angle is varied from 65° to 55°.

Figure 9.1 Effect of injection spray angle on CH₄ emissions with 80% diesel at 25NG case injected.

Figure 9.1 shows the effect of injection spray angle on CH₄ emissions with 80% diesel injection mass for 25NG case. Decreasing injection spray angle from 65 to 60 ° has no notable impact on CH₄ emissions. However, further decreasing spray angle beyond 60° was found to significantly decrease CH₄ emissions. The minimum CH₄ emissions of 14.7g/ kWh was observed at 57° spray angle. Further decreasing the injection spray angle started to significantly increase CH₄ emissions. This indicates that the diesel fuel injection spray angle has a significant impact on CH₄ combustion in an NG-diesel dual

fuel engine. In order to further investigate this effect, three representative computational cases with different diesel fuel injection spray angle are selected for further detailed examination, as shown in Table 9.1.

Table 9.1 Representative injection spray angle cases

Spray angle	Features
65°	Spray angle same with 25NG
57°	Lowest CH ₄ emission
55°	CH ₄ emission increases again

Figure 9.2 Spray momentum for three representative timings shown in Table 9.1.

Figure 9.3 Volume of 'pilot spray region' for three representative spray angle shown in Table 9.1.

Figures 9.2 and 9.3 shows the momentum and volume of ‘pilot spray region’ for three representative spray angles shown in Table 9.1. The spray momentum slightly increases and then decrease as spray angle decreased from 65° to 57° and then 55° . Accordingly, the volume of ‘spray region’ for 57° crank angle case is the highest among the three cases examined. The effect of spray angle on CH_4 emissions may also be affected by the shape and geometry of piston combustion chamber. The attenuation of spray momentum at 57° spray angle case is the weakest. This is supported by the distribution of mixture fraction larger than 0.01 and CH_4 at 10° and 50° CA ATDC for different diesel injection spray angles, as shown in Figures 9.4 and 9.5, respectively. The vector arrows in Figure 9.4 represent the velocity field. The diesel fuel for 57° spray angle case moves further toward the cylinder centerline than other two cases after impinged on piston and cylinder head. The area of the interface between the combustion products of diesel fuel and unburned methane-air mixture observed at 57° spray angle case is highest among all cases simulated as shown in Figure 9.5. This indicates the more CH_4 are burned at 57° spray angle than others. This also helps to burn more methane during post-combustion expansion process benefiting from the larger interface between hot combustion products and unburned methane-air mixture, and the higher momentum observed at 57° case shown in Figure 9.2.

Figure 9.4 Distributions of region where mixture fraction larger than 0.01 (1st row, colored by temperature) and CH₄ (2nd row, colored by CH₄ mole fraction) at 10° CA ATDC for different spray angles. The vector arrows indicate the velocity field.

Figure 9.5 Distributions of region where mixture fraction larger than 0.01 (1st row, colored by temperature) and CH₄ (2nd row, colored by CH₄ mole fraction) at 50° CA ATDC for different spray angles. The vector arrows indicate the velocity field.

9.2 Effect of multi-pulse injection on CH₄ combustion

The second objective in this chapter is to explore the potential of the multi-pulse pilot fuel injection strategies in reducing CH₄ emissions. In this sub-section, the simulation was conducted with fixed spray angle of 57° spray angle. The pre-pilot injection is applied for the 20% diesel mass in 25NG case with injection timing is varied from -50° to -10° CA ATDC while the main pilot (80% n-heptane) was injected at -7 °

CA ATDC The injection pressure and other boundary conditions such as intake temperature and pressure were kept the same with that in 25NG case. Figure 9.6 shows the effect of pre-pilot fuel injection timing on CH_4 emissions. The CH_4 emissions observed with pre-pilot diesel fuel injection (injection timings varied from -50° to -10° ATDC) are all lower than that for 25NG case. The CH_4 emissions monotonically decreases as pilot fuel injection timing advanced from -10° CA ATDC to -50° CA ATDC. The CH_4 emissions observed at -50° CA ATDC pilot fuel injection timing is 3.04 g/kWh , which is only 22.3% of that for 25NG case (13.61 g/kWh). The multi-pulse injection with advanced pre-pilot fuel injection strategy has significant advantage in reducing CH_4 emissions from NG-diesel dual fuel engines. In order to explore the mechanism of CH_4 emission reduction under multi-pulse injection, the computational case having -50° pilot fuel injection timing is selected for further detailed investigation.

Figure 9.6 Effect of pre-pilot injection timing on CH_4 emissions. 25NG case, Main pilot injection: fuel 80%, timing: -7° CA ATDC; Pre-pilot injection: diesel fuel: 20%, timing: -50° CA ATDC.

Figure 9.7 Effect of split injection strategies on spray momentum, spray angle: -57° . Main pilot injection: fuel 80%, timing: -7° CA ATDC; Pre-pilot injection: diesel fuel: 20%, timing: -50° CA ATDC.

Figure 9.7 compares the spray momentum between main injection only case and multi-pulse injection case simulated with -57° spray angle shown in Figure 9.1. Figures 9.8 and 9.9 show the distribution of isolated volume where mixture fraction larger than 0.01 representing the region where diesel fuel or its combustion product present and CH_4 for multi-pulse injection case. The pre-pilot diesel fuel injected at -50° CA ATDC reaches the piston bowl and in turn bounced back toward the flat platform of piston. The diesel injected during pre-pilot injection pulse mixed with CH_4/air mixture and ignited at around -10° CA ATDC. The diesel fuel injected in main pilot injection stage pushed the pre-pilot injected diesel/ CH_4/air mixture toward the piston centerline, which further increased the spray momentum compared to the single injection case as shown in Figure 9.7. The volume of the high temperature combustion products produced during the combustion for multi-pulse injection case is much larger than that observed with single injection strategies. As a result, more CH_4 -air mixture is consumed, leading to a lower CH_4 emissions observed

with multi-pulse injection operation than that observed with the single pilot fuel injection pulse (25NG case), as shown in Figure 9.10.

Figure 9.8 Distributions of region where mixture fraction larger than 0.01 (colored by temperature) at multi-pulse injection case at different crank angle.

Figure 9.9 Distributions of CH₄ (colored by CH₄ mole fraction) at multi-pulse injection case at different crank angle.

Figure 9.10 Distributions of isolated volume where mixture fraction larger than 0.01 (1st row, colored by temperature) and CH₄ (2nd row, colored by CH₄ mole fraction) at 50° CA ATDC for multi-pulse injection (top) and single injection pulse case (25NG) (bottom) case.

9.3 Summary

This chapter numerically explored the potential of spray angle and multi-pulse pilot injection strategy on CH₄ emissions from NG-diesel dual fuel engine. Two set of artificial simulation cases including spray angle and multi-pulse pilot fuel strategies were simulated. The spray momentum calculation was applied to quantify the in-cylinder momentum initiated by high injection pressure. Based on the simulation results obtained in this research, the following conclusions can be drawn:

(1) The spray momentum observed at 57° spray angle is the strongest among all single injection pulse cases simulated. More CH₄ is consumed during the combustion process and a lower CH₄ emission is achieved at 57° spray angle.

(2) The multi-pulse injection has a significant strong potential on CH₄ emissions reduction in NG-diesel dual fuel engine. With an advanced -50° CA pre-pilot fuel injection, the diesel/CH₄/air containing region was significantly increased, leading to a 77.7% reduction to CH₄ emissions at 25NG case.

Chapter 10 Conclusions

10.1 Conclusions

This research numerically investigates the combustion process and exhaust emissions from a NG-diesel dual fuel engine using CFD model CONVERGE coupled with a reduced PRF chemistry. A post-processing tool has been developed to calculate, analyze, and visualize the instantaneous ROP of key species in each cell with the known temperature, pressure, and species concentration exported by the CFD model. The ROP data is post-processed to derive the key reactions dominating the formation of CO, NO₂ and the consumption of CH₄ in a NG-diesel dual fuel engine. Based on the simulation work conducted in this research, the following conclusions can be drawn:

- The combustion of CH₄ in a NG-diesel dual fuel engine at low loads was dominated by the combustion of the pilot fuel, the relative volumetric ratio of pilot fuel vapor over the total volume, the movement of the hot combustion products towards the unburned mixture, and the mixing of the hot combustion products with the unburned CH₄-air mixture.
- The spray plume of the pilot fuel injected into the cylinder produced a high velocity field of the bulk gas under the guidance of the piston bowl shape, which helped the mixing of the hot combustion products with the unburned CH₄ and contributes most to CH₄ consumption during the combustion process. The main

combustion process consumed 43% to 53% of the total CH_4 in cylinder.

- The post-combustion oxidation of CH_4 occurred in the interface between the hot combustion products and the unburned pre-mixed NG-air mixture, which increased the temperature of CH_4 to that needed for its oxidation. The post-combustion process consumes 17% to 29% CH_4 .
- The unburned CH_4 observed at EVO was located mainly at the center of the cylinder. The portion of CH_4 present at the boundary layer near the cylinder liner was relatively small. The total CH_4 left unburned at EVO was 27 to 35% of the intake CH_4 at the low load case simulated
- The optimization of dual fuel engine design, operation and fuel injection strategies aiming to minimizing CH_4 emissions should focus on those capable of increasing the relative volume of the pilot fuel vapor or its combustion products or increasing the chance to mix with hot combustion products early in the expansion process when the temperature of the combustion products is still high.
- The increased NO_2 emitted from NG-diesel dual fuel engine was mainly formed in the interface region between the hot NO-containing combustion products and the cool, unburned CH_4 -air mixture during the post-combustion expansion process. The oxidation of the CH_4 provided the HO_2 needed for the conversion from NO to NO_2 . The low NO_2 emissions from diesel engine might be due to lack of HO_2 formed during post-combustion expansion process.

- The NO_2 formed within pilot fuel spray during the early combustion process was converted to NO due to the high temperature of the combustion products, and the complete consumption of HO_2 present with NO after the complete oxidation of the local CH_4 and n-heptane. The NO_2 observed at EVO was formed mainly in the post combustion expansion process.
- The HO_2 needed for the conversion from NO to NO_2 was formed during the CH_4 oxidation process through the reaction path: $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{HO}_2$. The reaction 54: $\text{HCO} + \text{O}_2 = \text{HO}_2 + \text{CO}$ provided 98% of the HO_2 formed in the particular case examined in this research. The backward reaction of $\text{OH} + \text{NO}_2 = \text{NO} + \text{HO}_2$ consumed 34% of HO_2 for the conversion from NO to NO_2 .
- The NO to NO_2 conversion reaction was dominated by the temperature of the mixture consisting of NO , CH_4 , O_2 , etc. In comparison, the impact of ER of gaseous fuel or concentration of CH_4 on the conversion reaction rate factor was negligible.
- The distribution of NO and NO_2 in the ER-T diagram confirmed that the NO_2 emitted from a NG-diesel dual fuel engine was mainly formed and distributed in the mixture with a relatively low temperature. This ruled out the possibility for the NO_2 formed in the hot combustion zone of the pilot fuel to survive until EVO.
- The NO_2 in a NG-diesel dual fuel engine can be formed in the $\text{RCR}_{\text{NO}_2\text{-O}}$ and $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ regions. The $\text{RCR}_{\text{NO}_2\text{-O}}$ region represents the formation of NO_2 in high-temperature combustion products during the main combustion stage of pilot fuel. The $\text{RCR}_{\text{NO}_2\text{-HO}_2}$ region represents the interface between the hot

NO-containing combustion products and the cool CH₄-containing unburned CH₄-air mixture. The increased NO₂ emissions from NG-diesel dual fuel engines are mainly formed in the RCR_{NO2}-HO₂ region.

- The HO₂ radical required for NO-NO₂ conversion in the RCR_{NO2}-HO₂ region is produced by the reaction pathway: CH₄→CH₃→CH₂O→HCO→HO₂. The presence of the RCR_{NO2}-HO₂ region contributes to the significantly increased NO₂ emissions from a NG-diesel dual fuel engine compared to a traditional diesel engine. The unburned CH₄/air that survives the main combustion stage provides the CH₄ source for the production of HO₂ leading to the formation of more NO₂ in NG-diesel dual fuel engines than traditional diesel engines.
- The O radical required for NO-NO₂ conversion in the RCR_{NO2}-O region is produced by the reaction pathway: HCO→H→O, through reaction R17 and R18 with HCO produced during the oxidation process of n-Heptane noted as C₇H₁₅→CH₂O→HCO→H→O→NO₂. The examination of the RRC reveals that the key factor causing R17 and R18 to dominate HCO and H radical consumption is the high temperature. Therefore, the RCR_{NO2}-O region is featured with high temperature and the presence of O₂. Meanwhile, the high temperature can promote the destruction of NO₂ to NO by R3 and R4. As a result, the NO₂ concentration in the RCR_{NO2}-O region is lower than that in the RCR_{NO2}-HO₂ region. In addition, the NO₂ eventually emitted from dual fuel engines is mainly formed in the RCR_{NO2}-HO₂ region.
- The NO₂ emission from a NG-diesel dual fuel engine is determined by the total volume of RCR_{NO2}-HO₂ region and R1 reaction rate in the RCR_{NO2}-HO₂ region.

Compared with the 25NG case, the 50NG case has comparable $RCR_{NO_2-HO_2}$ region volume but significantly lower R1 reaction rate due to the combined effect of various factors such as local temperature, CH_4 concentration, and interaction between hot NO-containing combustion products and cool CH_4 /air mixture. The volume and R1 reaction rate of the $RCR_{NO_2-HO_2}$ region observed in the 50NG and 75NG cases are both lower than the 25NG case.

- The CO in Region-H was mainly produced by incomplete combustion of the diesel fuel during the main combustion stage. In comparison, the CO in Region-L of the 25NG case was produced by slow oxidation of lean diesel fuel, and oxidation of NG when mixed with the combustion products of lean diesel-air mixture formed during the main combustion process.
- The CO formation/consumption in Region-H of the diesel-only and NG-diesel dual fuel combustion mode was dominated by the intense competition between the forward and reverse reaction $HCO=H+CO$ at the interface between the RDR_{CO-R1} region and the RCR_{CO-R1} region. The consumption of CO formed in Region-H was dominated by reaction $CO+OH=CO_2+H$ which is affected by the entrainment of O_2 -containing mixtures into the CO-containing region. The CO produced during the main combustion stage was consumed through $CO \rightarrow HCO \rightarrow CO \rightarrow CO_2+H \rightarrow OH$. The OH radicals enhances the CO consumption during the post-combustion expansion process.
- The CO formation/consumption mechanism in Region-H was similar for both diesel engine combustion and NG-diesel dual fuel combustion modes. The addition of NG to intake air weakened the reactivity in region-H by reducing the

temperature and concentration of the active radicals such as H and OH, leading to the weakened reaction loop in the $R_{DR_{CO}}-R_2$ region. Therefore, the CO formation or concentration in Region-H for dual fuel mode was higher than that for diesel combustion mode.

- The CO formation/consumption mechanism in Region-L for the diesel only mode and dual fuel mode was significantly different. The CO in Region-L of diesel-only mode was produced by lean diesel-air fuel mixture near the spray periphery. The CO formed was later consumed during the post combustion stage. However, the CO in Region-L of dual fuel mode was produced by co-oxidation of CH_4 /air mixture and lean diesel-air mixture and its combustion products, which significantly increase the formation of CO in Region-L of dual fuel engine.
- The CO formation/consumption mechanisms and the reactions dominating the heat release in Region-L of the dual fuel mode was significantly affected by the mixing of diesel combustion products with CH_4 /air mixture. At lean mixture ($R_{XR}-R_{10}/R_{XR}-R_{11}$), the net CO production rate was positive (creation) and the CO production was dominated by R_2 , while the heat release was dominated mainly by R_{10} and R_{11} . As mixture fraction gets higher ($R_{XR}-R_6$), the net CO production rate was negative (destruction), the CO consumption was dominated by R_4 , and the heat release was dominated by R_6 .
- The CO in Region-L of the 25NG case was formed by reaction pathway: $CH_4 \rightarrow CH_3 \rightarrow CH_2O \rightarrow HCO \rightarrow CO$ and consumed by R_2 . The CO from the NG-diesel dual fuel combustion mode was mainly formed during the mixing process of the extremely lean diesel fuel and its combustion products with CH_4 /air

mixture where the local temperature was able to initiate the oxidation of CH_4 to CO , but too low to produce OH radical necessary for the consumption of CO through R2.

- The spray momentum observed at 57° spray angle is the strongest among all single injection pulse cases simulated. More CH_4 is consumed during the combustion process and a lower CH_4 emission is achieved.
- The multi-pulse injection has a significant strong potential on CH_4 emissions reduction in NG-diesel dual fuel engine. With an advanced -50° CA pilot fuel injection, the diesel/ CH_4 /air containing region was significantly increased, leading to a 77.7% reduction to CH_4 emissions at 25NG case.

10.2 Future work

The ROP data during combustion process can only be analyzed in 0D model in the past decades. The post processing tool developed in this research make the kinetics analysis in 3D CFD model available. For spray combustion where mixing plays a significantly important role, the research regarding the instantaneous information during the combustion process is limited. To explore the deeper understanding regarding IC engine combustion and the potential to reduce the emissions including NO_x , PM, etc., the future works are listed below:

- 1) To establish and validate a high fidelity LES model regarding spray combustion,

using n-heptane and n-dodecane as fuel.

- 2) To investigate the effect of air-entrainment on chemical kinetics process during the spray combustion process using the validated CFD model.
- 3) To investigate the transportation budget terms of important species during the combustion process using the validated CFD model.
- 4) To further develop and optimize the post processing tool developed in this research.

Appendix I Theory of Kinetics Calculation

This chapter presents important chemical reaction rate expressions [71] that are calculated in the CONVERGE SAGE model.

Consider elementary reversible (or irreversible) reactions involving K chemical species that can be represented in the general form:

$$\sum_{k=1}^K v'_{ki} \chi_k \rightleftharpoons \sum_{k=1}^K v''_{ki} \chi_k \quad (i = 1, \dots, I) \quad (\text{a-1})$$

The stoichiometric coefficients v_{ki} are integer numbers and χ_k is the chemical symbol for the k th species. the superscript ' indicates forward stoichiometric coefficients, while '' indicates reverse stoichiometric coefficients. Normally, an elementary reaction involves only three or four species; hence the v_{ki} matrix is quite sparse for a large set of reactions. for non-elementary reactions, equation (a-1) also represents the reaction expression, but the stoichiometric coefficients may be non-integers.

The production rate $\dot{\omega}$ of the k th species can be written as a summation of the rate-of-progress variables for all reactions involving the k th species:

$$\dot{\omega}_k = \sum_{i=1}^I v_{ki} q_i \quad (k = 1, \dots, K) \quad (\text{a-2})$$

Where

$$v_{ki} = v''_{ki} - v'_{ki} \quad (\text{a-3})$$

The rate of progress variable q_i for the i th reaction is given by the difference of

the forward and reverse rates as

$$q_i = k_{fi} \prod_{k=1}^K X_k^{v'_{ki}} - k_{ri} \prod_{k=1}^K X_k^{v''_{ki}} \quad (\text{a-4})$$

where v_{ki} is the stoichiometric coefficients, superscript ' indicates forward stoichiometric coefficients and '' indicates reverse stoichiometric coefficients; i indicates the index of i^{th} reaction, while k indicates index of the k^{th} species; X_k is the molar concentration of the k^{th} species; k_{fi} and k_{ri} are the forward and reverse RRC of the i^{th} reaction, respectively, calculated by Arrhenius expression.

The forward rate constants for the I reactions are generally assumed to have the following Arrhenius temperature dependence:

$$k_{fi} = A_i T^{\beta_i} \exp\left(\frac{-E_i}{R_c T}\right) \quad (\text{a-5})$$

Where the pre-exponential factor A_i , the temperature exponent β_i , and the activation energy E_i are specified by chemical kinetics mechanism. These three parameters are required input to the CONVERGE SAGE model. In equation (a-5), T refers to the gas temperature, unless auxiliary reaction information is provided to indicate that the reaction depends on a temperature associated with a particular species.

In thermal systems, the reverse rate constants k_{ri} are related to the forward rate constants through the equilibrium constants by

$$k_{ri} = \frac{k_{fi}}{K_{ci}} \quad (\text{a-6})$$

Although K_{ci} is given in concentration units, the equilibrium constants are more

easily determined from the thermodynamic properties in pressure units; they are related by

$$K_{ci} = K_{pi} \left(\frac{P_{atm}}{RT} \right)^{\sum_{k=1}^K \nu_{ki}} \quad (\text{a-7})$$

The equilibrium constants K_{pi} are obtained with the relationship

$$K_{pi} = \exp \left(\frac{\Delta S_i^o}{R} - \frac{\Delta H_i^o}{RT} \right) \quad (\text{a-8})$$

The Δ refers to the change that occurs in passing completely from reactants to products in the *ith* reaction.

Appendix II Reduced PRF Mechanism

$\text{C}_2\text{H}_2 + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$
 $\text{C}_2\text{H}_3 + \text{OH} = \text{C}_2\text{H}_2 + \text{H}_2\text{O}$
 $\text{C}_2\text{H}_3 + \text{CH}_2 = \text{C}_2\text{H}_2 + \text{CH}_3$
 $2\text{C}_2\text{H}_3 = \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4$
 $\text{C}_2\text{H}_3 + \text{O} = \text{C}_2\text{H}_2 + \text{OH}$
 $\text{C}_2\text{H}_2 + \text{OH} = \text{CH}_3 + \text{CO}$
 $\text{C}_2\text{H}_3 = \text{C}_2\text{H}_2 + \text{H}$
 $\text{C}_3\text{H}_6 + \text{H} = \text{C}_3\text{H}_5 + \text{H}_2$
 $\text{C}_3\text{H}_6 + \text{O}_2 = \text{C}_3\text{H}_5 + \text{HO}_2$
 $\text{CH}_2\text{CHO} + \text{H} = \text{CH}_3 + \text{HCO}$
 $\text{CH}_2\text{O} + \text{O}_2 = \text{HCO} + \text{HO}_2$
 $\text{CH}_2\text{O} + \text{O} = \text{HCO} + \text{OH}$
 $\text{CH}_2\text{O} + \text{H} = \text{H}_2 + \text{HCO}$
 $\text{CH}_2\text{O} + \text{M} = \text{CO} + \text{H}_2 + \text{M}$
 $\text{CH}_2\text{O} + \text{M} = \text{H} + \text{HCO} + \text{M}$
 $\text{HCO} + \text{OH} = \text{CO} + \text{H}_2\text{O}$
 $\text{HCO} + \text{O} = \text{CO} + \text{OH}$
 $\text{HCO} + \text{O} = \text{CO}_2 + \text{H}$
 $\text{HCO} + \text{HO}_2 = \text{CO}_2 + \text{H} + \text{OH}$
 $\text{C}_2\text{H}_6 + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{CH}_4$
 $\text{C}_2\text{H}_6 + \text{H} = \text{C}_2\text{H}_5 + \text{H}_2$
 $\text{CH}_3 + \text{O}_2 + \text{M} = \text{CH}_3\text{O}_2 + \text{M}$
 $\text{CH}_3 + \text{CH}_3\text{O}_2 = 2\text{CH}_3\text{O}$
 $\text{CH}_3\text{O}_2 + \text{O} = \text{CH}_3\text{O} + \text{O}_2$
 $\text{CH}_3\text{O}_2 + \text{H} = \text{CH}_3\text{O} + \text{OH}$
 $\text{CH}_3\text{O} + \text{H} = \text{CH}_3 + \text{OH}$
 $\text{CH}_3 + \text{O} = \text{CH}_2\text{O} + \text{H}$
 $\text{CH}_3 + \text{O}_2 = \text{CH}_3\text{O} + \text{O}$
 $\text{CH}_3 + \text{H}(+\text{M}) = \text{CH}_4(+\text{M})$
 $\text{CH}_3\text{O}_2\text{H} = \text{CH}_3\text{O} + \text{OH}$
 $\text{CH}_2\text{O} + \text{CH}_3\text{O}_2 = \text{CH}_3\text{O}_2\text{H} + \text{HCO}$
 $\text{C}_2\text{H}_4 + \text{CH}_3\text{O}_2 = \text{C}_2\text{H}_3 + \text{CH}_3\text{O}_2\text{H}$
 $\text{CH}_3\text{O}_2 + \text{CH}_4 = \text{CH}_3 + \text{CH}_3\text{O}_2\text{H}$
 $\text{CH}_3\text{O}_2 + \text{HO}_2 = \text{CH}_3\text{O}_2\text{H} + \text{O}_2$

$\text{C}_2\text{H}_6 + \text{OH} = \text{C}_2\text{H}_5 + \text{H}_2\text{O}$
 $\text{C}_2\text{H}_6 + \text{O} = \text{C}_2\text{H}_5 + \text{OH}$
 $2\text{CH}_3(+\text{M}) = \text{C}_2\text{H}_6(+\text{M})$
 $\text{C}_2\text{H}_6 + \text{O}_2 = \text{C}_2\text{H}_5 + \text{HO}_2$
 $\text{C}_2\text{H}_6 + \text{HO}_2 = \text{C}_2\text{H}_5 + \text{H}_2\text{O}_2$
 $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 = 2\text{C}_2\text{H}_5$
 $\text{C}_2\text{H}_6 + \text{M} = \text{C}_2\text{H}_5 + \text{H} + \text{M}$
 $\text{C}_2\text{H}_6 + \text{CH}_2 = \text{C}_2\text{H}_5 + \text{CH}_3$
 $\text{C}_2\text{H}_6 + \text{CH}_3\text{O}_2 = \text{C}_2\text{H}_5 + \text{CH}_3\text{O}_2\text{H}$
 $\text{C}_2\text{H}_5 + \text{C}_3\text{H}_6 = \text{C}_2\text{H}_6 + \text{C}_3\text{H}_5$
 $\text{C}_2\text{H}_5 + \text{C}_3\text{H}_5 = \text{C}_2\text{H}_6 + \text{C}_3\text{H}_4$
 $\text{C}_2\text{H}_4 + \text{O} = \text{CH}_2\text{CHO} + \text{H}$
 $\text{C}_2\text{H}_3 + \text{O}_2 = \text{CH}_2\text{CHO} + \text{O}$
 $\text{CH}_2\text{CHO} + \text{O}_2 = \text{CH}_2\text{O} + \text{CO} + \text{OH}$
 $\text{C}_2\text{H}_2 + \text{OH} = \text{CH}_2\text{CO} + \text{H}$
 $\text{CH}_2\text{CO} + \text{H} = \text{CH}_3 + \text{CO}$
 $\text{CH}_2\text{CO} + \text{O} = \text{CH}_2 + \text{CO}_2$
 $\text{CH}_2\text{CO}(+\text{M}) = \text{CH}_2 + \text{CO}(+\text{M})$
 $\text{C}_3\text{H}_6 + \text{O} = \text{CH}_2\text{CO} + \text{CH}_3 + \text{H}$
 $\text{CH}_2\text{CHO} = \text{CH}_2\text{CO} + \text{H}$

Appendix III Reduced GRI NO_x Mechanism

Appendix IV CHEMKIN source code

KK: number of species

II: number of reactions.

P: pressure

T: temperature

D: mole fraction matrix.

IWORK: Array of integer workspace in CHEMKIN.

WORK: Array of real work space in CHEMKIN.

%calculate progress variable (Q)

CALL CKQXP(P,T,D,IWORK,WORK,Q)

%calculate the contribution of reactions to species (CIK), and export.

OPEN(2,FILE='ckcont.dat')

DO i=1,KK

CALL CKCONT(i,Q,IWORK,WORK,CIK)

write(2,100)CIK

ENDDO

CLOSE(2)

%calculate the creation and destruction of species (CDOT and DDOT), and export.

CALL CKCDXP(P,T,D,IWORK,WORK,CDOT,DDOT)

OPEN(2,FILE='CD_DOT.dat')

DO i=1,KK

write(2,100)CDOT(i),DDOT(i)

ENDDO

CLOSE(2)

%calculate the forward and reverse rate of reactions (FWDK and REVK), and export

CALL CKKFKR(P,T,D,IWORK,WORK,FWDK,REVK)

OPEN(2,FILE='FRRR.dat')

DO i=1,II

write(2,100),FWDK(i),REVK(i)

ENDDO

CLOSE(2)

Appendix V Detailed GRI NO_x mechanism

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