Effect of Hydrogen Addition on Diesel Engine Operation and NO\textsubscript{x} Emission: A Thermodynamic Study

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Abstract: Problem statement: The worldwide increasing energy demand and the environmental problem due to greenhouse gas emission, especially produced from fossil fuel combustion, have promoted research work to solve these crises. Diesel engine has proven to be one of the most effective energy conversion systems. It is widely used for power generation, land vehicles and marine power plant. To reduce diesel fuel consumption, an alternative energy sources, such as Hydrogen (H\textsubscript{2}), is promoted to use as dual-fuel system. H\textsubscript{2} is considered as a fuel for future because it is more environmental friendly compared to carbon-based fuel. However, the most exiting diesel engines were designed for using diesel fuel. Feeding H\textsubscript{2}-diesel dual fuel to the engine, it is required to study its effect on engine operation parameters. Moreover, it is also an interesting point to observe the engine emission when H\textsubscript{2}-diesel dual fuel is used. Approach: The thermodynamic modeling was used to simulate the operating parameters, i.e., cylinder pressure and gas temperature. Finite different method was employed to find the solution. The H\textsubscript{2} supply and EGR were varied. The pressure and temperature were observed. For NO\textsubscript{x} emission, which is a major problem for use of diesel engine, the thermodynamic equilibrium calculation was conducted to find the mole fraction of gas species in the exhaust gas. The mole fraction of NO and NO\textsubscript{2} were combined to present as the mole fraction of NO\textsubscript{x}. Results: The simulation showed that at 5% EGR, increase of H\textsubscript{2} caused increasing of cylinder pressure and temperature. It also increased NO\textsubscript{x} in exhaust gas. However, when H\textsubscript{2} was fixed at 10%, increasing EGR led reducing of cylinder pressure and temperature. The mole fraction of NO\textsubscript{x} decreased with increasing EGR. Conclusion: The H\textsubscript{2} supplied to the engine provided positive effect on the engine power indicated by increasing pressure and temperature. However, it showed the negative effect on NO\textsubscript{x} emission. Use of EGR was recommended for controlling NO\textsubscript{x} emission when H\textsubscript{2} is supplied.

Key words: Thermodynamic modeling, nitrogen oxide, dual-fuel, hydrogen, diesel engine, Hydrogen (H\textsubscript{2}), Exhaust Gas Recirculation (EGR)

INTRODUCTION

Due to energy crisis and environmental problem, more efficient and cleaner engines have been developed. Diesel engines are widely used, especially for transportation and power generation because of their higher thermal efficiency. However, it is well known that NO\textsubscript{x} and smoke emissions are the important problems for use of diesel engine. Therefore, many researches have been done in order to improve diesel engines efficiency and lower their emission. One of the most frequently used methods to control NO\textsubscript{x} is supplying Exhaust Gas Recirculation (EGR) into the intake manifold of engine. Maiboom et al. (2008) investigated the effect of EGR on the diesel engine emission. They found that EGR was more effective way to control NO\textsubscript{x} emission. The simulation of NO\textsubscript{x} formation in diesel engine has been done. The NO\textsubscript{x} emission at different equivalence ratio, which was predestined by the single zone zero dimensional model, agreed with the experimental results.

Hydrogen is one of the most promising energy carriers fulfilling energy, environment and sustainable development needs. Since hydrogen is a carbon-free fuel, hydrogen combustion does not generate CO\textsubscript{2} and smoke (Miyamoto et al., 2011). Using hydrogen and diesel fuel in diesel engine, called dual-fuel diesel engine, it has been interested by many researchers. Varde and Frame (1983) studies the effect of hydrogen added in the intake of a diesel engine. The result showed that smoke decreased with the increase in hydrogen addition. Dual-fuel operation of biodiesel with hydrogen was studied by Geo et al. (2008). They found that NO\textsubscript{x} emission increased with increase in

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hydrogen. The diesel engine combustion process and knocking behavior was investigated by Szwaja and 
Grab-Rogalinski (2009) when the proportion of 
hydrogen and diesel fuel was varied. They reported that 
the hydrogen addition affected the ignition delay. The 
simulation of exhaust emission for diesel engine using 
diesel blended with hydrogen was conducted by 
Masood and Ishart (2008). The conclusion of their 
study showed that NO\textsubscript{x} emission was depended on the 
equivalent ratio.

In this study, the thermodynamic simulation for 
diesel engine was developed. The amount of H\textsubscript{2} supply 
was varied while the fraction of Exhaust Gas 
Recirculation (EGR) was fixed in order to study the 
effect of H\textsubscript{2} on the engine operation parameters i.e., 
cylinder pressure and temperature and NO\textsubscript{x} emission. 
To investigate the effect of EGR on hydrogen-diesel 
dual fuel engine, the amount of EGR was changed and 
H\textsubscript{2} supply was fixed. The cylinder pressure and gas 
temperature were found. The effect of EGR at constant 
H\textsubscript{2} supply was also observed in this study.

**MATERIALS AND METHODS**

To find the Pressure (P) and the Temperature (T) of 
working fluid in the engine cylinder, the first law of 
thermodynamics for closed system was applied and it 
can be expressed as:

\[
\begin{align*}
\frac{dQ_{in}}{dt} + \frac{dQ_{out}}{dt} - P \frac{dV}{dt} + U & = 0
\end{align*}
\]  \hfill (1)

where, Q and U represent heat and internal energy, 
respectively. For the ideal gas, the differentiation of 
internal energy, shown on the right side of Eq. 1, can be 
written as:

\[
\frac{dU}{dt} = mc, \quad \frac{dT}{dt}
\]  \hfill (2)

Considering the equation of state, a differentiation 
of gas temperature can be obtained as:

\[
\frac{dT}{dt} = \frac{1}{mR} d(PV)
\]  \hfill (3)

where, R is the gas constant. Substituting Eq. 3 into Eq. 
2, it leads to the following equation:

\[
\frac{dU}{dt} = \frac{c_v}{R} \left( P \frac{dV}{dt} + V \frac{dP}{dt} \right)
\]  \hfill (4)

By substituting Eq. 4 into Eq. 1, the following 
equation is obtained.

\[
\frac{dQ_{in}}{dt} \frac{dQ_{out}}{dt} - \frac{dP}{dt} \frac{dV}{dt} + \frac{c_v}{R} \left( P \frac{dV}{dt} + V \frac{dP}{dt} \right)
\]  \hfill (5)

Using chain rule of differentiation, Eq. 5 can be 
rewritten as:

\[
\frac{dQ_{in}}{dt} \frac{dQ_{out}}{dt} - \frac{dP}{dt} \frac{dV}{dt} = \frac{c_v}{R} \left( P \frac{dV}{dt} + V \frac{dP}{dt} \right)
\]  \hfill (6)

where, \( \theta \) is the crank angle and \( \frac{d\theta}{dt} = \omega \) is the crank 
age angular velocity which is related to the engine 
speed. Rearranging Eq. 6, it is finally obtained an 
equation describing the relationship between the 
cylinder pressure and the crank angle as Eq. 7:

\[
\frac{dP(0)}{d\theta} = \frac{\gamma-1}{V(0)} \left( \frac{dQ_{in}}{d\theta} - \frac{\dot{Q}_{out}}{\gamma} \right) - \frac{\gamma}{V(0)} \frac{dV(0)}{d\theta}
\]  \hfill (7)

where, \( \gamma \) is the specific heat ratio (\( \gamma = c_p/c_v \)). The heat 
release rate due to combustion of fuel, \( \frac{dQ_{in}}{d\theta} \), can be 
calculated by using Eq. 8 (Gogio and Baruah, 2010):

\[
\frac{dQ_{in}}{d\theta} = Q_\text{LHV} \frac{dx_n}{d\theta}
\]  \hfill (8)

where, \( x_n \) is the mass fraction burned obtained from the 
Weibe function which is defined as:

\[
x_n = 1 - \exp \left[ -a \left( \frac{\theta - \theta_{sc}}{\Delta \theta} \right)^{m+1} \right]
\]  \hfill (9)

where, \( \theta_{sc} \) is the start of combustion and \( \Delta \theta \) is the 
combustion duration. \( a \) and \( m \) are the parameters that 
characterizes the combustion process in the engine 
cylinder. In Eq. 9, the coefficients \( a \) and \( m \) are 5.0 and 
2.0, respectively (Ferguson and Kirkpatrick, 2001). For 
rate of heat transfer from gas in cylinder to cylinder 
wall, \( \frac{\dot{Q}_{out}}{\omega} \), it can be estimated by using Eq. 10:

\[
\frac{\dot{Q}_{out}}{\omega} = h \left( A(\theta) - T(\theta) - T_w \right)
\]  \hfill (10)

The convective heat transfer coefficient, \( h \), is 
expressed as shown in Eq. 11 (Heywood, 1988):
Table 1: Engine geometry and operational conditions used in simulation

| Parameter                          | Value             |
|------------------------------------|-------------------|
| Cylinder bore [m]                  | 8.75×10⁻²         |
| Stroke [m]                         | 1.1×10⁻¹          |
| Connecting rod length [m]          | 2.34×10⁻³         |
| Clearance volume [m³]              | 5.50×10⁻⁶         |
| Engine speed [rpm]                 | 2,000             |
| Air Fuel ratio [-]                 | 1.1               |
| Injection timing [degree BTDC]     | -20               |
| Wall temperature [K]               | 450               |

\[ h_g = 3.26D^{0.2}P^{0.5}T^{0.55}w^{0.8} \] (11)

where, \( w \) is the velocity of the burned gas given by Eq. 12:

\[ w = c_1 S_p + c_2 \frac{V_t T_r}{P_r V_d} (P(\theta) - P_n) \] (12)

The coefficient \( c_1 = 2.28 \) whereas \( c_2 = 0 \) during the compression process and \( c_2 = 0.00324 \) during the combustion and the expansion processes. \( S_p \) is the piston speed. \( V_d \) is the displacement volume. The quantities \( V_n, T_r, \) and \( P_r \) are reference state properties at closing of inlet valve and \( P_m \) is the pressure value in cranking.

The instantaneous cylinder volume, area and displacement are given as Eqs. 13-15, respectively:

\[ V(\theta) = V_0 + \frac{\pi D^2}{4} X(\theta) \] (13)

\[ A(\theta) = \frac{\pi D^2}{4} + \frac{\pi D S}{2} \left( a + 1 - \cos \theta + \left( a^2 - \sin^2 \theta \right)^{1/2} \right) \] (14)

\[ X(\theta) = (L + a) \left( 1 - \cos \theta + \frac{1}{2} \left( L^2 - \sin^2 \theta \right)^{1/2} \right) \] (15)

where, \( a \) is crank radius, \( S \) is stoke and \( L \) is connecting rod length.

For the working fluid temperature, the calculation was done by using Eq. 16, which is derived from the ideal gas equation of state.

\[ T(\theta) = \frac{P(\theta)V(\theta)}{m R} \] (16)

In this study, the interested result is not only the thermodynamic state, represented by pressure and temperature, but also the chemical compositions of exhaust gas. To show the effect of added hydrogen and EGR on the engine emission, the thermodynamic equilibrium method based on the minimization of Gibbs free energy described in Ref. (Jarungthammachote, 2011) was used. This method is based on that at equilibrium state, the total Gibbs free energy of the system is minimized. The total Gibbs free energy of system is defined in Eq. 17:

\[ G_i = \sum_{i=1}^{N} n_i G_i = \sum_{i=1}^{N} n_i \mu_i \] (17)

where, \( n_i \) and \( \mu_i \) are the number of moles and the chemical potential of species \( i \), respectively. \( G_i \) represents the partial molar Gibbs free energy of species \( i \).

If all gases are assumed as ideal gas, the chemical potential of species \( i \) can be obtained from Eq. 18:

\[ \mu_i = \Delta G_i^{\text{f, i}} + RT \ln \{ y_i \} \] (18)

where, \( R \) and \( T \) are the universal gas constant and temperature, respectively. \( y_i \) is The mole fraction of gas species \( i \) and it is the ratio of \( n_i \) and the total number of moles in the reaction mixture. \( \Delta G_i^{\text{f, i}} \) represents the standard Gibbs free of formation of species \( i \). The Lagrange multiplier method is conducted with constraint of mass balance, i.e.:

\[ \sum_{i=1}^{N} a_{ij} n_i = A_j, j = 1,2,3,...,k \] (19)

where, \( a_{ij} \) is the number of atom of the \( j \)-th element in a mole of the \( i \)-th species. \( A_j \) is defined as the total number of atom of \( j \)-th element in the reaction mixture.

The solutions \( n_i \) have to be real numbers in the boundary such that \( 0 \leq n_i \leq n_{\text{hot}} \). In this study, there are the number of mole of \( \text{CH}_4, \text{CO}, \text{CO}_2, \text{H}_2, \text{H}_2\text{O}, \text{O}_2, \text{N}_2, \text{NO} \) and \( \text{NO}_2 \). The summation of \( \text{NO} \) and \( \text{NO}_2 \) is presented in terms of \( \text{NO}_x \). The Newton-Raphson method is used to find the solution. The data from Jarungthammachote (2011) is employed to calculate all thermodynamic properties in this model.

The engine and operational conditions used in this simulation are presented in Table 1. The thermal properties of diesel fuel, ignition delay and duration of combustion were assumed following the information obtained from (Heywood, 1988).

**RESULTS**

The simulation results were obtained by solving Eq. 7 which is differential equation. The numerical method called finite difference technique was employed. The mole fraction of fed hydrogen was varied while the EGR was fixed. Then, the results were observed.
To investigate the effect of EGR on the engine operation and emission, the amount of hydrogen was fixed and the mole fraction of EGR was changed. The results of simulation are given in Fig. 1-6. Figure 1 and 2 present the effect of hydrogen supply on cylinder pressure and gas temperature, respectively. For the effect of EGR, Fig. 3 and 4 shows the cylinder pressure and gas temperature, respectively at different EGR rates. The last two figures elucidate the variation of NOx due to the change of hydrogen supply and EGR.
DISCUSSION

In the first case, EGR was fixed at 5% and H\textsubscript{2} supply was varied. From the simulation results, Fig. 1 and 2 clearly show that increasing H\textsubscript{2} supply causes increase of cylinder pressure and temperature. As shown in Fig. 1 the peak of cylinder pressure is 6.4 MPa for 5% H\textsubscript{2} supply while 20% H\textsubscript{2} supply raises the peak of pressure up to 8.0 MPa. As observed from the simulation results, for each 5% increase of H\textsubscript{2} supply, the peak of cylinder pressure gains about 490 kPa. For the gas temperature, it can be increased with increasing H\textsubscript{2} supply. The peak of gas temperature for 5% H\textsubscript{2} supply is about 1700 K and it reaches 2120 K when H\textsubscript{2} is fed with 20%. 5% H\textsubscript{2} fed into engine can increase the peak of gas temperature about 140 K. From the results, it can be explained that more H\textsubscript{2} induced into the cylinder increases releasing energy from combustion process. Thus, combustion gas has higher pressure and temperature.
The relationship between cylinder pressure and EGR is expressed in Fig. 3. The H₂ supply was fixed at 10% while EGR was varied from 5-20%. The result shows that the cylinder pressure decreases with increasing EGR. The same effect can be observed for the gas temperature. Reduction of gas temperature is found when EGR fraction is increased, as presented in Fig. 4. From the results, it can be implied that EGR acts as combustion dilutor. Most of gas species in EGR do not react with H₂ and diesel fuel.

To study NOₓ emission, chemical equilibrium calculation was simultaneously done with pressure and temperature simulation. Figure 5 indicates that NOₓ fraction in exhaust gas increases with increasing H₂ supply. At 20% H₂ supply, the NOₓ emission is higher than that at 5% H₂ supply with 2500%. This is the effect of rising temperature due to increasing H₂ supply. The same effect was observed by Varde and Frame (1983). Miyamoto et al. (2011) demonstrated that at the energy per cycle of 0.9 kW/cycle, NO first decreased, attained minimum at 4% of H₂ supply and then NO increased with increasing H₂ supply. In contrast, increase of EGR reduces the NOₓ emission, as shown in Fig. 6, because EGR lower the gas temperature. Comparing with NOₓ emission at 20% H₂ supply, it is 1400% lower than that at %5 H₂ supply.

**CONCLUSION**

In this study, the thermodynamic model for diesel engine was developed to simulate the effects of H₂ addition and EGR on the operation condition and NOₓ emission. The chemical equilibrium method was used to find the mole fraction of NOₓ in the exhaust. The result showed that increasing H₂ caused increases of cylinder pressure and temperature. Therefore, the NOₓ emission was grown due to increasing temperature. Therefore, it should be make sure that the engine structure can handle the increasing pressure and the engine cooling system can control the temperature to protect the overheat.
damage. In contrast, EGR could reduce the cylinder pressure and temperature. To control NOx emission, use of higher EGR was recommended to diesel engine added H2 to the intake air.

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