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Reformed Exhaust Gas Recirculation Products of Rapeseed-based Biodiesel: A Chemical Equilibrium Simulation

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Abstract

This paper simulates the products from an exhaust gas fuel reforming of rapeseed methyl ester (RME) in comparison with ultra-low sulphur diesel (ULSD). Both types of fuel were also correspondingly used as reformer fuels. In all cases, the reactor inlet temperature was kept constant at 300°C which represents exhaust gas temperature at low load engine condition and is comparable to the actual average exhaust gas temperature. The gas hourly space velocity (GHSV) was set-up at 30,000 h^{-1} and 45,000 h^{-1} whereas the latter is a half of typical value for automotive three-way catalytic converters. Different fuel flow rates between 25 and 55 $ml \cdot h^{-1}$ were tested. The reforming products and temperatures were calculated using an equilibrium model. The results have shown that different engine and reforming fuels affect the produced reformed gasses. Reforming of RME produced less hydrogen compared to the ULSD reforming. The results from simulation were compared with those from experiment at the same condition. At the higher GHSV, an offset between the measured experimental results and the predicted results from the equilibrium model has been found for all conditions tested. For the lower GHSV, the equilibrium model enables a good prediction in reforming yields of hydrogen.

Keywords : Biodiesel, Equilibrium, Exhaust gas fuel reforming, Hydrogen, Simulation

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1. Introduction

An issue concerning the nitrogen oxides (NO_x) and particulate matter (PM) trade-off emissions is vitally being solved by a number of researchers with various methods, e. g. fuel properties and engine technologies. For instance, the use of biodiesel blends as fuels for diesel engines tends to increase NO_x emissions while substantially reduce PM with comparable engine thermal efficiency [1-3].

For these reasons, a reformed exhaust gas stream rich in hydrogen, using direct catalytic interaction of hydrocarbon fuel with partial exhaust gases in sufficient high temperature with oxygen and steam, is proposed to be added into the engine intake, called reformed exhaust gas recirculation (REGR) [4]. It is subsequently to form a homogeneous charge pre-mixed with fresh air to lower combustion temperature, thus generating less NO_x emissions, while avoiding the increase in PM typical in diesel engine exhaust gas recirculation [5]. Therefore, a way to produce hydrogen on-board is to use exhaust gas-assisted fuel reforming instead of carrying a massive hydrogen vessel in a vehicle [6]. For further understanding, the engine-exhaust gas reformer system is depicted in Fig. 1.

Furthermore, the use of appropriate proportions of reformer fuel and water added to reformer raises reactions that result in higher level of hydrogen production [7]. When considering engine-reformer close-loop operation, substituting part of the main engine fuel with hydrogen-rich gas resulted in improved fuel economy at middle and high load condition although fuel addition to the reformer to produce REGR is required [8].

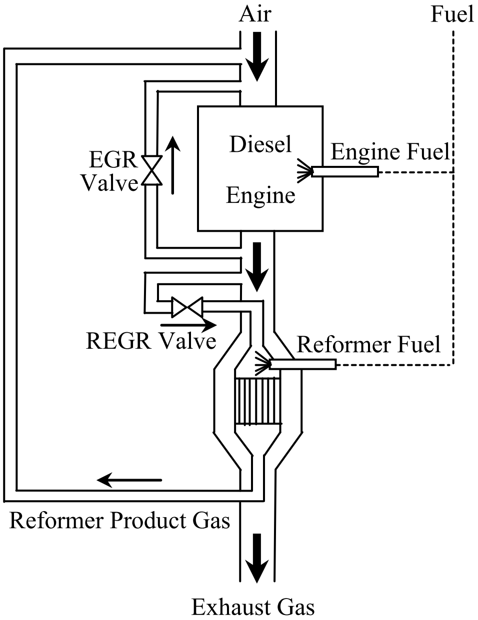

Fig. 1. The engine-reformer system

Due to exhaustive experimental accomplishment, in the present study, the effects of engine fuel and reforming fuel with different compositions on the reformed exhaust gas composition are revealed using an in-house chemical equilibrium simulation. Furthermore, the model verification is also carried out with corresponding results from experiment as well as the influences of exhaust gas dosing in terms of gas hourly space velocity have been examined and discussed.

2. Reactions concerning fuel reforming

In automotive applications, hydrogen generation can be accomplished by a combination of major reforming techniques for both exothermic and endothermic reactions. The exothermic reactions comprise partial or complete oxidation, water-gas-shift reaction, and auto-thermal reforming, respectively shown in Eq. (1) to (4) by which the endothermic reaction is associated with steam reforming described in Eq. (5) [6].

$$C_xH_yO_z+\left(\frac{x}{2}-\frac{z}{2}\right)O_2 \rightarrow xCO+\frac{y}{2}H_2 \qquad (1)$$

$$C_xH_yO_z+\left(x+\frac{y}{4}-\frac{z}{2}\right)O_2 \rightarrow xCO_2+\frac{y}{2}H_2O \qquad (2)$$

$$CO+H_2O \leftrightarrow CO_2+H_2 \qquad (3)$$

$$C_xH_yO_z+\left(x-\frac{z}{4}-\frac{1}{2}\right)O_2+H_2O \rightarrow xCO_2+\left(\frac{y}{2}+1\right)H_2 \qquad (4)$$

$$C_xH_yO_z+(x-z)H_2O \rightarrow xCO+\left(x+\frac{y}{2}-z\right)H_2 \qquad (5)$$

Partial oxidation is an alternative method for producing hydrogen from fuels at sub-stoichiometric oxygen-to-fuel ratio. The limited oxygen amount confines the fuel oxidation. But, the process is not benefit in terms of efficiency owing to its inherently exothermal reaction. Complete oxidation may occur, depending on the reactor conditions and prejudice the hydrogen production. Via the water-gas-shift reaction [9], carbon monoxide from the steam reforming can combine with excess steam to produce further hydrogen at temperature below 750°C. In auto-thermal reforming, the partial oxidation and steam reforming reactions proceed in a reformer by feeding the fuel, steam and oxygen together into the catalytic reactor. Steam reforming is a common method for commercial bulk hydrogen production at high temperatures of up to 1100°C in the presence of a catalyst. This process is very industrious under strong endothermic reaction [10]. In effect, the steam reforming reaction which absorbs part of the heat generated by the oxidation limits the peak temperature in the reactor and the overall reaction is a slightly exothermic process [10].

3. Thermodynamic analysis of the exhaust gas fuel reforming

The thermodynamic analysis of the exhaust gas fuel reforming of ultra-low sulphur (ULSD) and rapeseed methyl ester (RME), formerly presented in [11], are used to compare a fuel capability to improve heating value and concisely state hereafter. Throughout the reforming study, the ULSD and RME containing overall carbon to hydrogen ratio (by mass) of 6.43 and 6.51 respectively are used as fresh reforming fuels. Due to the lack of the precise thermodynamic properties of ULSD and RME, their standard enthalpies of formation are assumed to be the same as those of cetane [12] and methyl octadecanoate [13] respectively, since fuel properties are comparable. All standard enthalpies of formation at 1 atmosphere and 298 K used to calculate the heats of reaction are given in [12-13]. Water content in the present equations are in the gas phase while the standard enthalpies of formation of the elements H_2, O_2, and N_2 are zero by definition.

In this work, both engine fuel and reformer fuel are the same. The exhaust gas from the engine is from the combustion of ULSD with air (Eq. 6). The subsequent exhaust gas partly flows through the catalytic reformer where a portion of ULSD was injected to mix and react with, to produce the reformed hydrogen rich fuel (Eq. 7). Lastly, the reformed fuel produced earlier was combusted with air (Eq. 8).

(i) Stoichiometric combustion of 1 kmol of ULSD

$$C_{15}H_{28}+22(O_2+3.76N_2)\longrightarrow 15CO_2+14H_2O+82.72N_2 \quad (6)$$

with the heat of reaction $Q_{PR,298(i)} = 8,840$ MJ

(ii) Reforming of 1 kmol of ULSD using exhaust gases from (i) above

$$C_{15}H_{28}+0.52(15CO_2+14H_2O+82.72N_2) \longrightarrow 22.88CO+21.28H_2+43.01N_2 \quad (7)$$

with the heat of reaction $Q_{PR,298(ii)} = -2,756$ MJ

(iii) Stoichiometric combustion of reformed fuel produced in (ii)

$$22.88CO+21.28H_2+43.01N_2+22(O_2+3.76N_2) \longrightarrow 1.52(15CO_2+14H_2O+82.72N_2) \quad (8)$$

with the heat of reaction $Q_{PR,298(iii)} = 11,596$ MJ

From the ideal analysis, it is apparent that:

$$Q_{PR,298(i)} - Q_{PR,298(ii)} = Q_{PR,298(iii)}$$
$$8,840-(-2,756) = 11,596 \text{ MJ/kmol } C_{15}H_{28}$$

In the reforming step (ii), the negative sign of the heat of reaction calculated from Eq. 7 indicates that the sufficient energy of 2,756 MJ/kmol is required for the reforming process. Theoretically, the reformed fuel releases 11,596 MJ/kmol of reforming fuel, as compared to 8,840 MJ/kmol from the combustion of the main engine fuel.

A definition of the reactor thermal efficiency given in [4] is the ratio of heating value of reformed fuel and heating value of main engine fuel, approximately equal to the heat of reaction ratio. In this case, the reactor thermal efficiency of the ULSD engine-reformer system will be:

$$\eta_{R,th} = \frac{11,596}{8,840} \times 100 = 131.2\% \quad (9)$$

which represents an improvement in fuel heating value of 31.2%.

In the same manner, the calculation is repeated for neat RME as the engine main fuel and reforming fuel.

(i) Stoichiometric combustion of 1 kmol of RME

$$C_{19}H_{35}O_2+26.75(O_2+3.76N_2) \longrightarrow 19CO_2+17.5H_2O+100.58N_2 \qquad (10)$$

with the heat of reaction $Q_{PR,298(i)}$ = 10,938 MJ

(ii) Reforming of 1 kmol of RME using exhaust gases from (i) above

$$C_{19}H_{35}O_2+0.47(19CO_2+17.5H_2O+100.58N_2) \longrightarrow 28.09CO+25.73H_2+47.27N_2 \qquad (11)$$

with the heat of reaction $Q_{PR,298(ii)}$ = -3,175 MJ

(iii) Stoichiometric combustion of reformed fuel produced in (ii)

$$28.09CO+25.73H_2+47.27N_2+26.75(O_2+3.76N_2) \longrightarrow 1.47(19CO_2+17.5H_2O+100.58N_2) \qquad (12)$$

with the heat of reaction $Q_{PR,298(iii)}$ = 14,113 MJ

Again, from the ideal analysis, it is apparent that:

$$Q_{PR,298(i)} - Q_{PR,298(ii)} = Q_{PR,298(iii)}$$

$$10{,}938-(-3{,}175) = 14{,}113 \text{ MJ/kmol } C_{19}H_{35}O_2$$

In this case, the reactor thermal efficiency of the RME engine-reformer system will be:

$$\eta_{R,th}=\frac{14{,}113}{10{,}938}\times 100 = 129.0\% \qquad (13)$$

which represents an improvement in fuel heating value of 29.0%.

4. Materials and methods

4.1 Chemical equilibrium analysis

The catalytic combustion of exhaust gas and fuel was studied and simulated through the chemical equilibrium method. The concept of Gibbs free energy minimisation combined with the energy balance was used. The amount of added fuel was varied to study the parameters mentioned. In all cases, the compositions of exhaust gas i.e. carbon dioxide (CO_2), carbon monoxide (CO), steam (H_2O), hydrogen (H_2), nitrogen (N_2), oxygen (O_2) and hydrocarbon (HC, represented as CH_4) were calculated. The amount of each gas species can be obtained by balancing in molar basis.

The method is based on equilibrium state that the total Gibbs free energy of the system has minimum value. For the multi-reaction, single phase system, the total Gibbs free energy (G^t) can be expressed as Eq. (14):

$$G^t=\sum_{i=1}^{N} n_i g_i \qquad (14)$$

where g_i and n_i are the chemical potential and the number of mole of specie i, respectively. Therefore, the total Gibbs free energy for the system of assumingly ideal gas can be calculated using Eq. (15):

$$G^t=\sum_{i=1}^{N} n_i \Delta\overline{G}^0_{f,i} = \sum_{i=1}^{N} n_i \overline{R}T\ln\left(\frac{n_i}{n_{tot}}\right) \qquad (15)$$

where $\Delta\overline{G}^0_{f,i}$ is the standard Gibbs free of formation of species i and $\overline{R}$ is the universal gas constant.

To find the minimum value of G^t, the Lagrange multipliers optimisation is used. The mass balance of each chemical element is carried out and it is set as the constraint to this problem, yielding Eq. (16):

$$\Delta\overline{G}^0_{f,i}+\overline{R}T\ln\left(\frac{n_i}{n_{tot}}\right)+\sum_k \prod_k a_{ik}=0 \qquad (16)$$

where a_{ik} is the number of atom of the k^{th} element in a mole of the i^{th} species. The values of Π_k represent the Lagrange multipliers. The desired solution can be achieved by solving Eq. (16) with constraint equations.

To predict the combustion temperature on an adiabatic assumption, the energy balance is formed as Eq. (17):

$$\sum_R n_R\,\overline{H}_R(T_R)=\sum_P n_P\,\overline{H}_P(T_P) \qquad (17)$$

where $\overline{H}_R$ and $\overline{H}_P$ represent the enthalpies of reactants and products, respectively. The combustion temperature (T_p) is implicitly obtained from the enthalpy of product mixture following the calculation flowchart depicted in Fig. 2.

4.2 Experiment preparation

Instrument and other facilities formerly presented in [6] are used for validating the model and concisely state here as the followings.

4.2.1 Exhaust gas measurement

Exhaust gases containing CO, CO_2, HC and O_2 were measured before and after the reformer on a dry basis using an AVL DiGAS 440 analyser. A Hewlett Packard gas chromatograph equipped with thermal conductivity detector and argon as carrier gas in combination with a HP 3395 integrator were used to measure hydrogen content of the reformer products reading from the area of H_2 chromatogram.

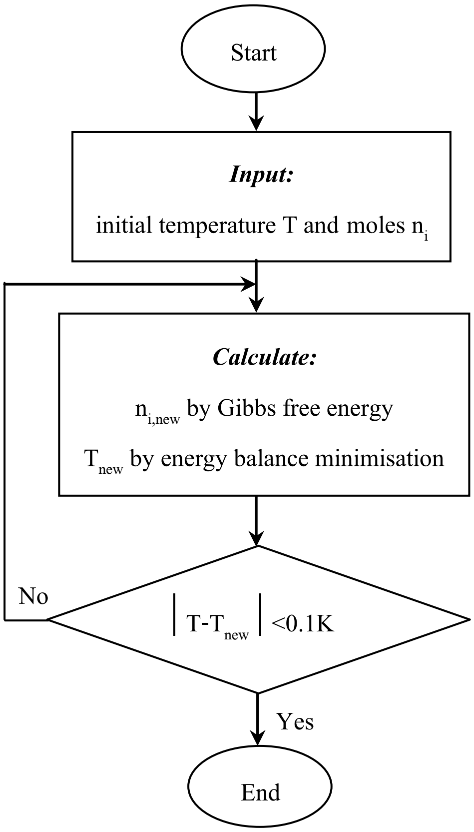

Fig. 2. Species and temperature calculation flowchart

4.2.2 Emission source

Exhaust gas emissions were from a V6 turbo-charged direct injection diesel engine MY 2005 equipped with a common rail fuel injection system. The key engine specification are as follows: bore 81.0 mm, stroke 88.0 mm, displacement volume 2,720 cm^3, compression ratio 17.3, maximum power 152 kW at 4,000 rpm and maximum torque 435 Nm at 1,900 rpm.

Table 1 Fuel properties [3]

Fuel analysis	ULSD	RME
Cetane number	53.9	54.7
LHV ($MJ{\cdot}kg^{-1}$)	42.7	39.0
Density at 15°C ($kg{\cdot}m^{-3}$)	827.1	883.7
Viscosity at 40°C (cSt)	2.467	4.478
Sulphur ($mg{\cdot}kg^{-1}$)	46	5
Empirical formula	$C_{15}H_{28}$	$C_{19}H_{35}O_2$

4.2.3 Test fuel

Ultra-low sulphur diesel (ULSD) and rapeseed methyl ester (RME), supplied by Shell Global Solutions UK were used in this study and their key properties are shown in Table 1.

4.2.4 Exhaust gas fuel reforming system

The engine exhaust gas flowed to a mini reformer through a 0.25-in diameter stainless steel tube and regulated by a rotameter. A precious metal-based 3-cm length monolith catalyst provided by Johnson Matthey was used in the test. It was loaded into the reformer with 1.5-cm diameter at 10 cm downstream of reformer inlet to promote uniform flow of reactant exhaust gases. The reformer was positioned in a cylindrical hollow furnace with a temperature controller to regulate gas temperature at the reformer inlet. A glass syringe type pump controlled liquid reforming fuel flow to the reformer well before the catalyst allowing fuel to completely evaporate and entrain with the reactants.

4.2.5 Experimental procedure

A steady-state engine operation of 10% load at 1500 rpm without exhaust gas recirculation (EGR) produced exhaust gases. In each experiment, the engine fuel and the reformer fuel were correspondingly the same type. The engine exhaust gas flow into the reformer was at the rate of 4 $l{\cdot}min^{-1}$. The gas hourly space velocity (GHSV, defined by volumetric flow rate of gas per hour divided by the volume of the monolith) was approximately 30,000 and 45,000 h^{-1}, which the latter is a half of typical value for automotive three-way catalytic converters. Reformer fuel flow rates were set at 25, 35, 45 and 55 $ml{\cdot}h^{-1}$ and for all conditions tested, the reformer inlet temperature was set to 300°C which is comparable to the actual average exhaust gas temperature at exhaust manifold.

5. Results and discussion

5.1 Effects of fuels on reforming products

Fig. 3 shows the simulation results of reformer produced gas composition when the engine was fuelled by ULSD and RME for the four different reformer fuel flow rates with 4 l•min^{-1} flow of exhaust gas, 45000 h^{-1} GHSV and 300°C inlet temperature. For both fuels, the increasing fuel flow rate resulted in an increase of H_2, CO and HC contents of the reformer product. The O_2 consumption and CO_2 production are believed to be due to complete oxidation of some fuel supplied to the reformer as reported in an earlier experimental study [5]. The un-reacted HC increased with increasing fuel flow but they are combustible and will be oxidised in the engine chamber in an engine-reformer closed loop system.

The simulated H_2 produced in the exhaust gas fuel reformer from the RME reforming contained up to 21% less hydrogen compared to ULSD reforming (Fig. 3). Up to 15% hydrogen content of the reformer product was attained from ULSD reforming. The amount of hydrogen production is affected by H/C atomic ratio of the fuel molecule. Theoretically the higher H/C of the ULSD molecule (1.856, compared to 1.848 for RME) benefits higher hydrogen yield [9] while the difference in reactant flow such as steam and oxygen contents of exhaust gas is yet of other parameters involved.

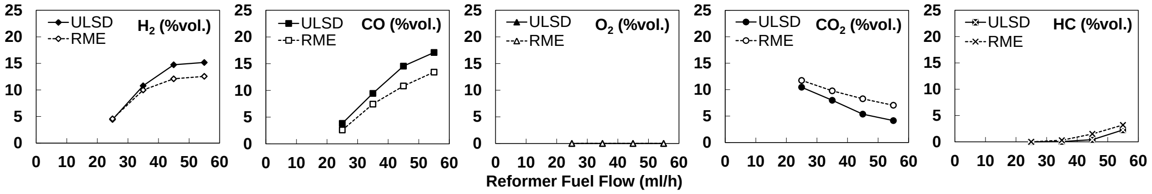

Fig. 3. Simulated REGR compositions at 45,000 h^{-1} GHSV and 300^{o}C reformer temperature

5.2 Model verification

Experimental results found in [6] were compared with predicted compositions obtained from the chemical equilibrium model at 45,000 h^{-1} GHSV for validation as shown in Fig. 4. At all conditions presented, the results from experiment and simulation are in good agreement while the experimental H_2 and CO yields were lower than those from the prediction, within 2% volumetric differences. This suggests that the reforming process may not reach the full equilibrium potential.

5.3 Influences of gas hourly space velocity

The experimental results from the reduction of GHSV down to 30,000 h^{-1} were also compared to the yields of hydrogen and carbon monoxide with predictions from the equilibrium model (Fig. 5). These trends of REGR product comparison are also the same as for the higher GHSV of 45,000 h^{-1}. It can be seen that the H_2 content of the reformer product is now much closer to the equilibrium simulation. When adding more reformer fuels, the experimental yields of CO were observed to tail off the predicted equilibrium.

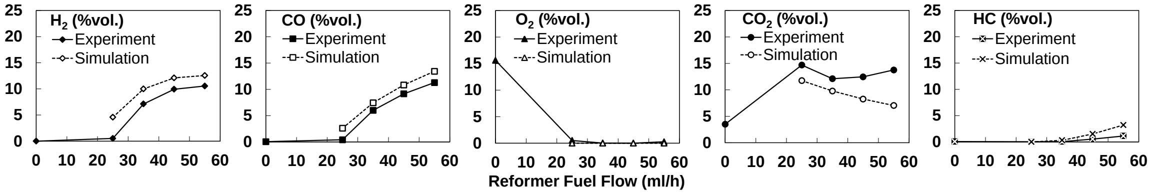

Fig. 4. Experiment and simulation comparison of REGR composition of RME at 45,000 h^{-1} GHSV

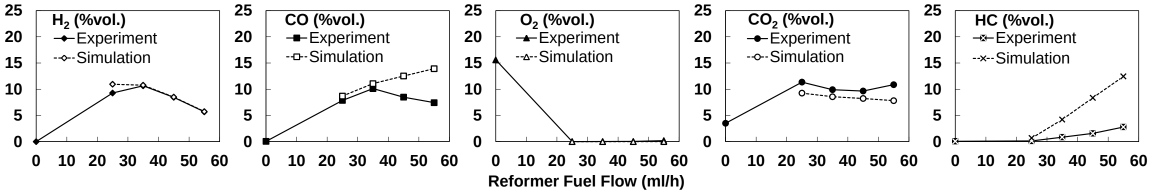

Fig. 5. Experiment and simulation comparison of REGR composition of RME at 30,000 h^{-1} GHSV

In this study, the catalyst bed length-to-diameter ratio of the experiment at 45,000 h^{-1} GHSV may not be a suitable value. Therefore, in the experiment, a radial reforming gas mixing and heat dissipation can potentially occur. In effects, some experimental results may differ from the equilibrium model where the simplified zero dimension are assumed.

6. Conclusion

The chemical equilibrium simulation of the exhaust gas fuel reforming process has shown that the differences in engine and reformer fuel affect the reformed gasses produced. Reforming RME produces lesser hydrogen than the ULSD reforming. The results from experiment and simulation are in-line but the experimental H_2 and CO yields were subtle lower than those from the prediction. For the lower GHSV, the equilibrium model yields a closed prediction for hydrogen generation from REGR.

7. Acknowledgement

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