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Biogas upgrading for on-board hydrogen production: Reforming process CFD modelling

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ARTICLE INFO

Article history:
Received 7 March 2014
Received in revised form
2 June 2014
Accepted 4 June 2014
Available online 4 July 2014

Keywords:
Biogas upgrade
Fuel reforming
Hydrogen
CFD
Reaction kinetics

ABSTRACT

Hydrogen production through fuel reforming can be used to improve IC (internal combustion) engines combustion characteristics and to lower vehicle emissions. In this study, a computational fluid dynamics (CFD) model based on a detailed kinetic mechanism was developed for exhaust gas reforming of biogas to synthetic gas (H_2 and CO). In agreement with experimental data, the reactor's physical and chemical performance was investigated at various O_2/CH_4 ratios and gas hourly space velocities (GHSV). The numerical results imply that methane reforming reactions are strongly sensitive to O_2/CH_4 ratio and engine exhaust gas temperature. It was also found that increasing GHSV results in lower hydrogen yield; since dry and steam reforming reactions are relatively slow and are both dependent on the flow residence time. Furthermore, the hot spot effect, which is associated to oxidation reforming reactions, was investigated for catalyst activity and durability.

Introduction

Biogas, which is produced through the anaerobic degradation of organic materials, can be used to reduce energy related pollution. Biogas typically contains 55–65% methane and 35–45% carbon dioxide (CO_2) and can be produced from different biomass waste and landfill materials [1]. Thus biogas has the advantage of being both clean and renewable along with an ease of implementation in existing power generating systems and to a less extent in transportation [2,3].

For automotive applications, biogas fuelled internal combustion (IC) engines can be used; however, in addition to challenges associated with on-board storage, they also suffer from combustion instability and high unburned methane emissions [4]. Moreover, the CO_2 content of the biogas, which dilutes the intake charge, limits the engine peak power due to the decrease in fuel calorific value. Several studies have reported that the addition of hydrogen to the intake mixture is beneficial for IC engines, since it can break the NO_x-particulate trade-off, promote auto-ignition, improve combustion stability and enhance after-treatment systems activity [5]. Since storing hydrogen is as yet impractical, attention has been recently given to on-board generation of hydrogen using reforming processes such as the exhaust gas reforming process proposed here (Fig. 1).

In this process, also known as REGR, exhaust gas heat is utilised to reform a mixture of fuel and exhaust gas into synthetic gas (H_2 and CO) over a precious metal catalyst. The hydrogen enriched gas is then injected into the engine manifold to be mixed with intake air. Several studies have proven that REGR improves combustion characteristics and decreases particulate and NO_x emissions, as well [5,6]. The inherent complexity of REGR requires appropriate modelling

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http://dx.doi.org/10.1016/j.ijhydene.2014.06.017

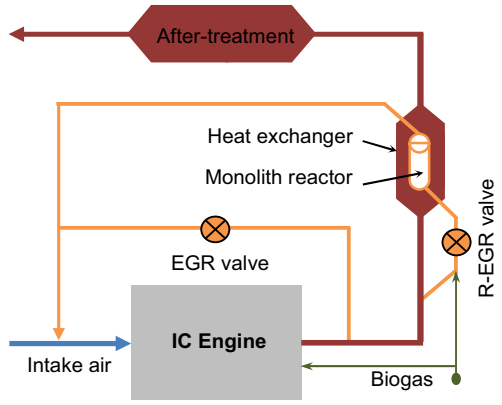

Fig. 1 – REGR diagram.

in order to optimise its implementation; this in turn requires a deep insight into the chemical and physical behaviour of its processes.

Fuel reforming reactions are complicated and still a matter of debate in the literature. Four main global reactions contribute to the catalytic reformation of methane; namely dry reforming (DRR, Eq. (1)); partial oxidation (POX, Eq. (2)); steam reforming (SRR, Eq. (3)) and water gas shift reaction (WGSR, Eq. (4)). Although methane SRR is the most versatile method for H_2 production, POX offers a promising alternative for automotive applications since its exothermic nature provides heat for accelerating other endothermic reactions. Furthermore, partial oxidation is a suitable process for small scale applications and allows a compact reactor design. On the other hand, in POX reactors, the presence of hot spots near the catalyst entrance can considerably affect the catalyst durability [7].

While the number of global reactions in methane reforming is limited, there are several elementary reactions that have to be taken into account for its accurate kinetic modelling. According to Dalle Nogare, "Since both exothermic and endothermic reactions are involved, a temperature variation does not translate directly to a reactant conversion, and energy and mass balance are deeply coupled" [8]. This indicates that computational fluid dynamics (CFD) is a valuable tool for reforming process modelling in comparison to plug flow reactor (PFR) models, where heat and mass transport is simplified excessively.

Dry reforming reaction

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (\Delta H_r = +260.6\ \text{kJ/mol}) \tag{1}$$

Partial oxidation reforming

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \quad (\Delta H_r = -22.63\ \text{kJ/mol}) \tag{2}$$

Steam reforming reaction

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (\Delta H_r = +226.8\ \text{kJ/mol}) \tag{3}$$

Water gas shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (\Delta H_r = -33.86\ \text{kJ/mol}) \tag{4}$$

To date, most research on methane reforming has been focused on applications related to fuel cell and fuel processing for instance Fischer–Tropsch and GTL (gas to liquid). Therefore hydrogen purity and optimizing H_2/CO ratio were the major parameters to consider [9]. However, in REGR there is a major difference which requires further investigation. The transient nature of the exhaust gas conditions requires a responsive design for an REGR reactor to obtain a satisfactory hydrogen yield. This can be achieved by understanding the effect of different key parameters such as O_2/CH_4 ratio, inlet temperature, etc.

In this study, a three dimensional CFD model for a heterogeneous POX reactor with a rhodium catalyst was developed. A detailed kinetic model, proposed by Deutschmann et al. was adapted for simulating the reforming surface reactions [10]. The model was validated with the experimental results published in our earlier work [11]. The validated model was used to investigate the overall performance of biogas reforming at various operating conditions. The effect of different O_2/CH_4 ratios was examined to optimize the exhaust gas (as the source of oxygen) contribution in the reactor feed gas. Moreover, the influence of gas hourly space velocity (GHSV, Eq. (5)) was also investigated in order to study the influence of various flow rates on the REGR system. Simulated operating conditions are detailed in Table 1.

$$\text{GHSV}(\text{h}^{-1}) = \frac{1}{\text{Residence time}} = \frac{\text{Feed flow rate } (\text{m}^3\ \text{h}^{-1})}{\text{Catalyst bed volume } (\text{m}^3)} \tag{5}$$

Methodology

Reactor geometry and CFD grid

The geometry of the model, which is illustrated schematically in Fig. 2, was created based on the monolith reactor used by Lau et al. [11]. The biogas reforming reactor was modelled as an isothermal heterogeneous reactor. It consists of two zones which are connected at an interface, namely a heat up zone and a monolith zone. The reactant temperature increases while passing through the non-reactive heat up zone. Inside the monolith zone reforming surface reactions occur with the presence of the rhodium catalyst.

For simulation purposes, only a single quarter of the geometry was modelled assuming horizontal and vertical symmetry planes at $x = 0$ and $y = 0$, respectively. The reactor wall is considered to be at a constant temperature (isothermal) since it was held within a large tube furnace in the experimental study [11]. It should be noted that in the REGR application, the reactor would be integrated in a heat exchanger to gain thermal energy from the main stream of the engine exhaust gas to accelerate the reforming reactions. The geometry was discretized into 25,680 structured hexagonal cells using the sweep method in ANSYS ICEM CFD software (ANSYS Inc.). Grid density was increased near the catalyst entrance where higher temperature and species gradients exist. To

Table 1 – Operating conditions for biogas reforming.

Parameter	Conditions			
GHSV (h^{-1})	16,500	25,500	32,500	
O_2/CH_4 molar ratio	0.18	0.25	0.37	0.50