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Hydrogen production from bioethanol fuel mixtures via exhaust heat recovery in diesel engines: a promising route towards more energy efficient road vehicles

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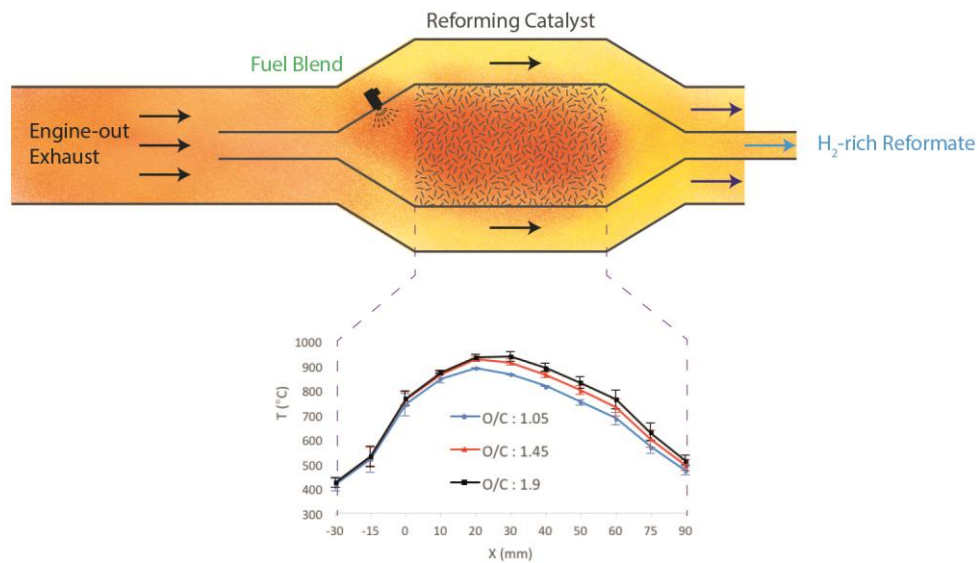
|| These authors contributed equally.

ABSTRACT

As a promising renewable fuel, bioethanol has been considered a potential alternative to the conventional fossil fuels in transportation sector and as a hydrogen (H₂) carrier. This study proposes a thermochemical recovery pathway to extend the use of bioethanol in compression ignition engines through catalytic exhaust gas reforming of ethanol-biodiesel-diesel blends into hydrogen. Through this, the aim is to improve the heat recovery of the engine exhaust gas and increase the on-board production of hydrogen which can potentially replace the diesel fuel in the engine. This would offer improved regulated emissions and reduced carbon footprint in road vehicles. Results indicate that the effectiveness of the reforming process and hydrogen production mainly depend on the blend composition, reforming temperature, and oxygen to carbon ratio (O/C). Also, ethanol content in the fuel blends proves to have a key role in sustaining catalyst activity and hydrogen production. It is deduced that a higher ethanol fraction promotes the reforming reactions as a result of its high hydrogen to carbon ratio, high reactivity, high enthalpy of vaporisation, shorter chain length, and its relatively high water content. Overall, the study highlights the positive impact and practicality of recovering exhaust heat using the ethanol-biodiesel-diesel blends. This implementation can result in noticeable improvements in emission reduction of diesel powertrains once the reformat is fed back into the engine.

Graphical abstract

Simplified catalytic exhaust gas reforming of ethanol-biodiesel-diesel blends into hydrogen



Keywords: Ethanol blends, hydrogen, heat recovery, reforming, biodiesel

Highlights

- Ethanol-diesel-biodiesel blends are effectively applied for producing H₂ on-board.
- Reforming the fuel blends is proven to be an effective thermochemical exhaust recovery method.
- H₂ from reforming is strongly dependant on fuel composition and injection conditions.
- Ethanol fraction in fuel blend has a dominant effect in reformer catalyst performance.
- Blends with higher ethanol and lower biodiesel fractions show a better recovery performance.

1. Introduction

Currently alternative fuels such as alcohols are being researched as partial replacements of diesel fuel, aiming fuel security, improved whole life-cycle CO₂ emissions, and reduction of the regulated pollutant emissions. The use of fuels with high bioethanol content is not recommended in compression ignition engines mainly due to its low auto-ignition tendency, poor lubricant properties, and its limited solubility with diesel fuels [1]. The use of ternary blends composed by ethanol-biodiesel-diesel has been proposed as the lubricity and solubility limitations of ethanol are compensated by the biodiesel. These blends offer an interesting

approach with proven tendency to reduce pollutant emissions without the NO_x penalty seen in biodiesel fuelling [2–5].

Catalytic exhaust gas reforming of conventional hydrocarbon fuels has been globally accepted as a promising route to produce hydrogen for vehicular applications [6–8]. Exhaust gas fuel reforming is the catalytic interaction of fuel with the exhaust gases, mainly H₂O and O₂, to produce hydrogen rich gas by utilizing excess waste heat of the engine exhaust. The composition of the reformed gas at the reactor exit is controlled by the reactor inlet feed ratio (O/C molar ratio) which also determines the extent of the reforming reactions [9]. The benefit of exhaust gas fuel reforming is that there is no need for the storage and supply of H₂O and O₂, thus hydrogen can be effectively produced on demand [10]. The use of reformat can aid the simultaneous control of engine output soot and NO_x emissions as well as to be used as a promoter for diesel aftertreatment units [9,11].

Fuel reforming of neat diesel type fuels [12–14], biodiesel [14–16], and ethanol [17–20] has been previously investigated. A low-temperature ethanol reforming pathway, catalysed by copper–nickel powder catalysts was investigated by Sall et al. [21]. The study focused on performance of various reformer reactors with different architectures. Introducing the best design, the study reports the feasibility of improving fuel economy and emissions in light-duty vehicles using onboard reforming of ethanol- or methanol-rich fuels. In another ethanol-based reforming study with exhaust heat from an internal combustion engine, performance of various catalytic honeycombs loaded by potassium-promoted cobalt hydrotalcite and with ceria-based rhodium–palladium were examined [22]. The results indicated that promotion of the ceria-supported noble metal catalyst with alumina and zirconia is a key element for practical application using commercial bioethanol. Showing an excellent stability and absence of carbon accumulation, the study concludes that Rh-Pd/Ce_{0.5}Zr_{0.5}O₂–Al₂O₃ catalyst was considered as a good candidate for practical on-board ethanol reforming. Another experimental study by Hwang et al. [23] investigated a novel thermally integrated steam reforming thermochemical recuperation reactor that used diesel engine exhaust energy for hydrous ethanol steam reforming. They concluded that using the heat recovery system for steam reforming of ethanol could lead to 23% increase in fuel heating value at 100% conversion, with compromise of increase in carbon monoxide and unburned hydrocarbon emissions. Several challenges arise from the use of heavy hydrocarbon components as those present in diesel. They have a limited diffusivity to reach the catalyst active sites and they could undergo thermal decomposition in the reformer to form coke [16]. Also, the presence of aromatic compounds in diesel fuel, which have high adsorption strength and low reactivity, can inhibit the reforming reactions [7,24–26].

Furthermore, diesel reforming generally requires high temperatures which can possibly lead to catalyst deactivation [6]. It happens because the high temperature can promote the breakage of C-C bond, forming carbon that will be deposited on the surface of the catalyst leading to its deactivation [14,27].

The addition of ethanol and biodiesel simultaneously could inhibit the formation and deposition of carbon on the surface catalyst thanks to their high oxygen content, but it has not been investigated yet under real exhaust gas conditions. Ethanol could also enhance catalyst activity to increase hydrogen production due to its high reactivity and diffusivity. Furthermore, ethanol tendency to absorbed water could locally increase the steam/carbon ratio which makes unfavourable conditions for coke formation [28].

The production of hydrogen enriched reformat through exhaust gas reforming from ethanol-biodiesel-diesel ternary fuel blends has been for the first time investigated through equilibrium and experimental methods using real engine exhaust gas. This proves to be a promising and practical way of recovering exhaust heat to further reduce the carbon footprint. In this investigation, temperature profiles along the catalyst, and the formation of H_2 , CO, CO_2 and THC in the product gas were evaluated.

2. Numerical and Experimental Methods

2.1 Test setup

The ethanol-biodiesel-diesel exhaust gas fuel reforming experiments were conducted in a laboratory reforming reactor using the real engine exhaust gas from an experimental single cylinder Lister Petter 1 diesel engine as shown in Figure. 1.

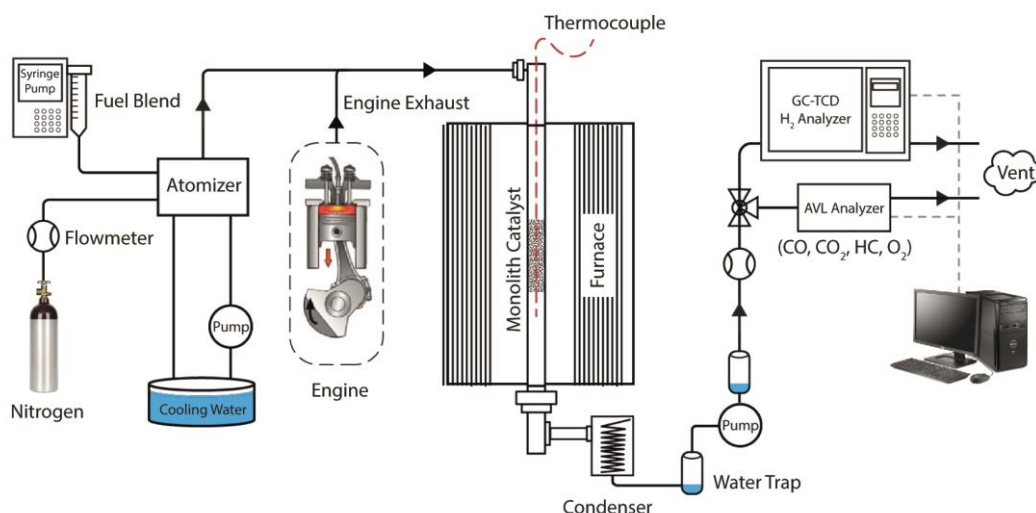


Figure 1. Schematic diagram of an exhaust gas fuel reforming system

The engine was run on neat diesel in all the cases and the exhaust gas was used in the reactor for the fuel reforming studies using different fuel blends. The reforming reactor was loaded with a monolith reforming catalyst developed by Johnson Matthey, with an aspect ratio ($AR = \text{length/diameter}$) of 2.95. The monolith catalyst consists of a high cell-density cordierite substrate (900 cells per square inch) which has been coated with 2%Pt-1%Rh (by mass) dispersed on a support containing 30% (by mass) ceria-zirconia (3:1 molar ratio) on 70% γ -alumina. A small core (25 mm diameter x 75 mm length) of the catalyst was placed inside a stainless-steel reactor that was held vertically within a large tube furnace.

The feed flow rate of both the fuel and the engine exhaust gas into the reforming reactor were controlled using volumetric flow meters. It is important to note that the nitrogen gas shown in the schematic is only used as an inert pressurising gas for fuel blend injection. A movable k-type thermocouple was used to measure the temperature profile along the catalyst, inside a channel at the centre of the monolith. The temperature of the exhaust gas entering the reactor was monitored using a thermocouple and external heat was provided by the furnace as a means of maintaining the temperature level similar to that of actual engine exhaust. Downstream of the reactor, the product gas was passed through the condenser and a water trap before the dry product gas was analysed. H_2 was measured using a Hewlett Packard (HP) gas chromatograph (GC) integrated with a thermal conductivity detector (TCD) and a HP integrator model 3395. The oven for the GC is temperature controlled and it is installed with two packed columns for hydrogen detection. Argon, which has a low thermal conductivity (0.024W/m/K) compared to

that of hydrogen (0.223 W/m/K) was introduced into the GC as a carrier gas. The analysis condition for the GC was set at 35 °C oven temperature and 100 °C detector temperature. The rest of the main gases including CO, CO₂, THC and O₂ were measured using an AVL Digas 440 non-dispersive infrared (ND-IR) analyser.

2.2 Experimental procedure

The fuels used for reforming process in this study were ultra-low sulphur diesel (ULSD), rapeseed methyl ester (RME) and bioethanol. The fuels were supplied by Shell Global Solutions UK and the fuels properties are shown in Table 1.

Table 1. Fuel Properties

Properties	Method	ULSD	RME	Ethanol
Molecular Formula		C ₁₄ H _{26.18}	C _{18.96} H _{35.29} O ₂	C ₂ H ₅ OH
Cetane Number	ASTM D613	53.9	54.7	5 – 8
Density at 15 °C (kg m ⁻³)	ASTM D4052	827.1	883.7	789
Viscosity at 40 °C (cSt)	ASTM D445	2.47	4.48	2.03
LHV (MJ kg ⁻¹)		42.49	36.86	26.83
Sulphur (mg kg ⁻¹)	ASTM D2622	46	5	0.7
Aromatics (% wt)		24.4	-	-
Water Content (mg.kg ⁻¹)	EN ISO2937	170	465	2000*
C (% wt)		86.46	77.18	52.17
H (% wt)		13.54	11.97	13.03
O (% wt)		-	10.85	34.78

* EN15489

In all the tests, the engine operating condition was 1500 rpm and 4 bar cylinder indicated mean effective pressure (IMEP). Table 2 shows the test conditions and exhaust gas composition.

Table 2. Test conditions and engine exhaust gas composition

Parameters	
Exhaust temperature (°C)	350
Reformer catalyst GHSV (h ⁻¹)	16,000
Reformer O/C molar ratios	1.05, 1.45, 1.90
Engine exhaust composition	
H ₂ O (%)	4.84

O ₂ (%)	13.9
N ₂ (%)	76.11
CO ₂ (%)	5.15
CO (ppm)	137
NO _x (ppm)	730
Soot (mg/m ³)	13
Total hydrocarbons (ppm)	330

The gas hourly space velocity (GHSV) was fixed at 16,000 h⁻¹ and it was calculated as shown in Eq. i.

$$GHSV(h^{-1}) = \frac{Feed\ Volume\ Flow\ Rate(m^3h^{-1})}{Catalyst\ Bed\ Volume(m^3)} \quad (i)$$

The value was chosen as the optimum GHSV for exhaust gas fuel reforming for on-board vehicle application according to reported values and previous experience [29]. For comparison of the different fuel blends the tests were carried out under the same O/C molar ratios: 1.05, 1.45 and 1.90, with taking into account the oxygen content in the fuel blends. For the reforming process, due to the lower energy density (energy per unit volume) of the ethanol, and its lower molecular weight, carbon, oxygen and hydrogen contents, the volumetric fuel flow was increased as the ethanol concentration in the blends is increased in order to achieve the same O/C ratios for all the considered fuel blends. Fuels were blended to form B30, B60, E5B30D65, E10B30D60, E15B30D55, E15B60D25, and E15B0D85 in order to study the dependence of reformer product gases on various biodiesel and ethanol concentrations. The volumetric composition (% vol.) of the fuel blends is illustrating in Figure 2. Also the properties of the different fuel blends are calculated based on the mixture compositions and presented in Table 3.

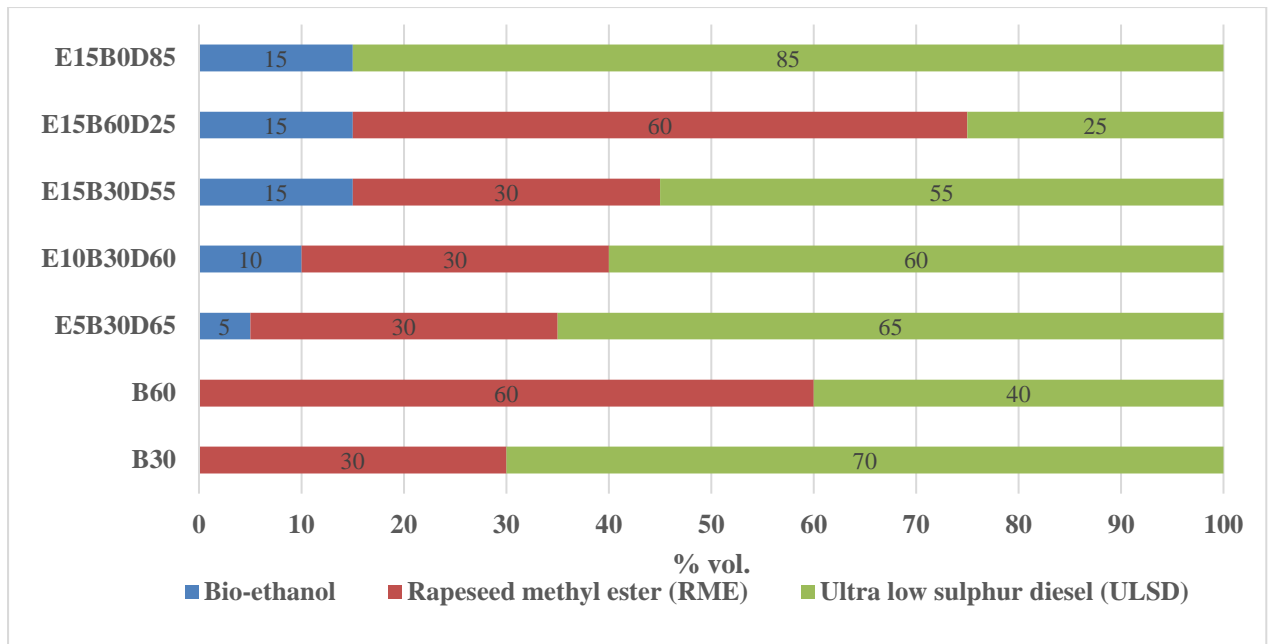


Figure 2. Volumetric composition of the fuel blends

Table 3. Properties of the studied fuel blends

Fuel Blend	Representative Molecular Formula	C/H molar ratio	Heat of Vaporisation (kJ/kg)	Heating Value (MJ/kg)	Power Input (J/sec)*
E0B60D40	$C_{16,54}H_{30,85}O_{1,02}$	0.536	228.45	39.98	506-958
E15B60D25	$C_{9,95}H_{19,62}O_{1,13}$	0.507	308.68	37.67	495-943
E0B30D70	$C_{15,15}H_{28,28}O_{0,46}$	0.535	239.01	41.61	499-926
E5B30D65	$C_{12,71}H_{24,16}O_{0,59}$	0.526	266.21	40.83	494-923
E10B30D60	$C_{10,88}H_{21,06}O_{0,68}$	0.516	293.52	40.05	489-914
E15B30D55	$C_{9,45}H_{18,65}O_{0,75}$	0.507	325.75	39.27	487-913
E15B0D85	$C_{9,01}H_{17,80}O_{0,41}$	0.506	336.25	40.93	472-859
E0B0D100	$C_{14}H_{26,18}$	0.535	250	43.3	489-883

* the range demonstrates the power input rate associated with the O/C range of 1.05-1.9.

2.3 Chemical equilibrium simulations

To examine the effect of bioethanol on reforming process with equilibrium perspective, a chemical equilibrium study is carried out. For this aim, the effect of ethanol addition on syngas composition, mainly H_2 and CO , is investigated by targeting diesel-ethanol fuel blends.

CHEMKIN Equilibrium Solver is used for the calculations. Detailed reaction mechanism by Westbrook et al [30] is applied with n-tetradecane as a diesel surrogate. All the reactor inlet parameters, such as the inlet temperature and exhaust composition, are set in accordance with the experimental study. Also, all the simulations are performed under constant pressure assumption. It is important to note that in all the equilibrium simulations only ethanol-diesel fuel blends are studied, due to accuracy compromise when applying reaction mechanisms for biodiesel surrogates.

3. Results and discussion

Equilibrium predictions

3.1 Effect of fuel composition on hydrogen production and temperature

Effects of reforming fuel composition on the final hydrogen levels as well as reforming temperature are illustrated for O/C ratio of 1.45 in Figure 3. The equilibrium simulations are evaluated in terms of ethanol content of the fuel blend. Overall trends indicate the higher yield of hydrogen for fuel blends with higher ethanol content. This is mainly due to the higher H/C ratio and reactivity of ethanol compared to diesel as well as the high heat of vaporisation and heat capacity of ethanol resulting in lower oxidation level for H₂. Equilibrium results show that for diesel-ethanol fuel blends with low ethanol content the reformer temperature is higher than that for high ethanol content fuel blends, leading to more dominant oxidation reactions. In other words, regarding the fuel properties of ethanol, the reactor temperature is more optimal for reforming when the ethanol content in the fuel blend exceeds a certain level. Up to 70%, with increasing ethanol fraction oxidation reactions dominate mainly due to more reactive nature of ethanol compared to diesel. As a result of this, hydrogen production decreases and temperature increases. On the other hand, because of the higher heat capacity of ethanol the temperature decreases. However, this decrease in temperature cannot compete with the increase of

temperature resulting from dominant oxidation reactions. It is observed that after replacing more than 70% ethanol, direction of the balance is changed dominating the effect of the high heat capacity of ethanol.

As reflected in the graphs, the predicted H_2 levels do not show a noticeable dependency on the ethanol content of the studied fuel blends within the range of 0-70% ethanol. There is only 3-5% difference in hydrogen yield along the whole interval. However, the experimental results indicate a stronger effect of the ethanol fraction on the resulted hydrogen levels, with the difference reaching up to 35%. The noticeable standard error in measured hydrogen level for pure ethanol case can be the outcome of some key factors: effect of catalyst in promoting specific reaction pathways, temperature distribution difference and active domain of exotherms and endotherms between the equilibrium predictions and experiments, and heat loss in experiments.

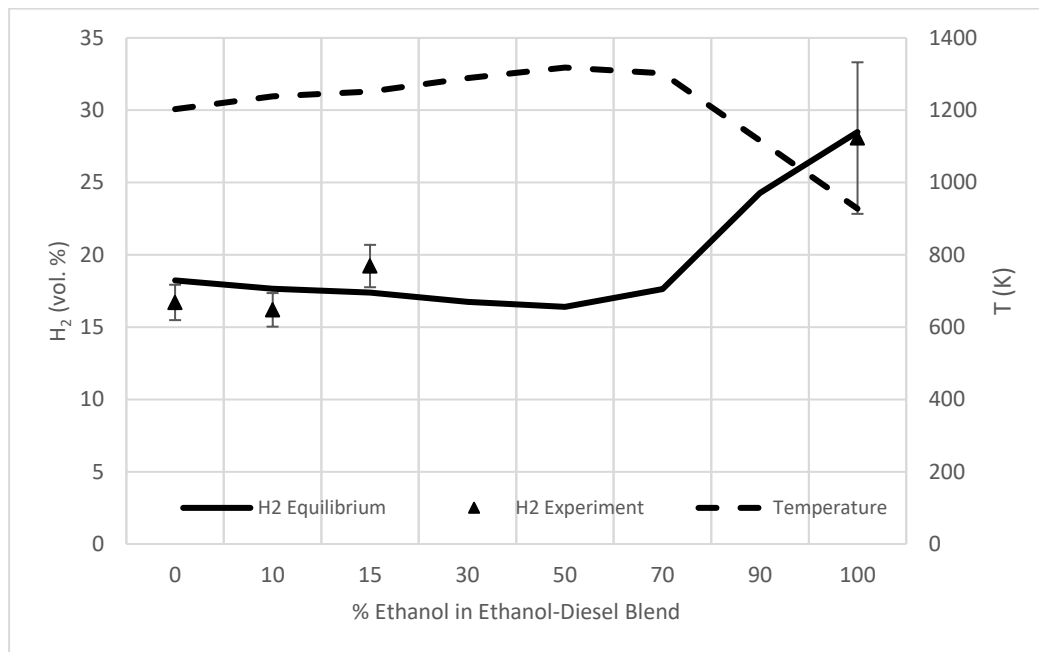


Figure 3. Effect of ethanol fraction of ethanol-diesel blends on hydrogen production and temperature, for O/C:1.45

Similar trends are observed for CO levels. As CO level generally increases experimentally with ethanol fraction of the blend, equilibrium simulations show minute changes, even decrease.

Regarding the discrepancies, it is of high importance to investigate the experimental phenomena which affects the reforming performance. The focus in the following sections will be on the various aspects of the experimental study for a wide range of ethanol-diesel-biodiesel fuel blends.

Experimental results

3.2 Effect of fuel blend on the temperature along the catalyst bed

Reaction temperature determines the magnitude and extent of the reforming reactions and hence the reactor gaseous products [31]. The variation of the temperature profiles along the catalyst bed is the reflection of the relative rates of exothermic and endothermic reactions taking place within the reactor, which in turn depend on several parameters such as O/C molar ratio, GHSV, and the fuel nature. Figure 4 shows the dependence of the reaction temperature on the O/C molar ratio for the E15B30D55 blend.

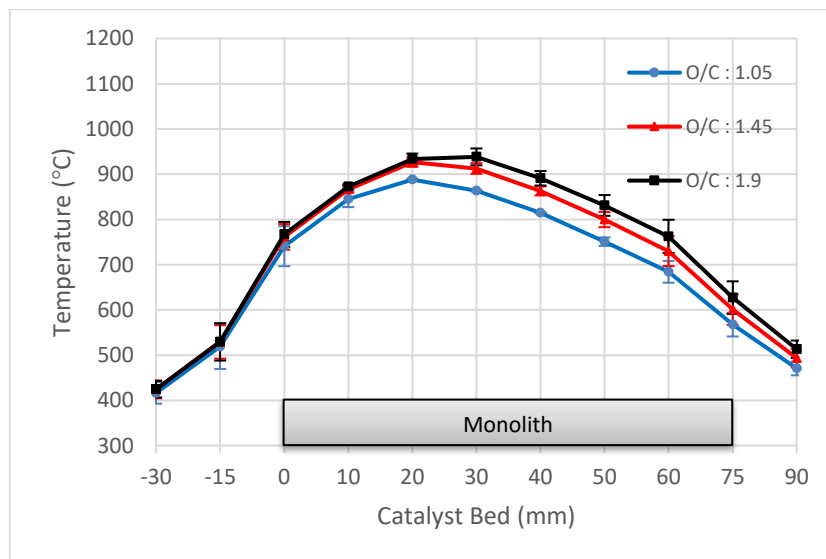


Figure 4. Effect of O/C molar ratios on temperature distribution along the catalyst bed for E15B30D55

As observed, there are two areas with different trends. In the first one there is an increase of the temperature and in the second area we can observe the decrease of this temperature along the catalyst bed. The rise in temperature is due to the oxidation (partial or complete) of the fuel taking place in the reactor to produce H_2O , CO_2 , H_2 and CO while depleting the oxygen,

resulting in generation of the heat and steam required for the endothermic SR reactions to occur. As the O/C molar ratio was increased, a wider exothermic region on the catalyst bed for the mixtures was seen. It is noteworthy that only the temperature profiles of the E15B30D55 blend are shown in the figure as representative examples, since similar behaviour in reaction temperature with respect to the O/C molar ratio was observed for all the studied fuel blends. Furthermore, it is important to note that the temperature prior to the catalyst bed is a result of the heat input from the furnace (catalyst is placed in the middle of the furnace) that mimics a typical diesel exhaust temperature and heat convection from the reaction zone to upstream of the catalyst. As expected, blends will have different temperatures at the entrance of the catalyst due to the difference in their heat capacities as well as slightly different temperature profiles along the reformer catalyst.

In order to understand the biodiesel effect on the temperature profile along the monolith, under the same O/C molar ratio two diesel-biodiesel blends (B30 and B60) and three ethanol-biodiesel-diesel blends with the same ethanol content of 15% (E15B0D85, E15B30D55, E15B60D25) are selected for study (Figure 5a). The temperature profile follows a similar trend for all the tested blends and the O/C molar ratios (only O/C of 1.05 shown here) i.e., a sharp rise in temperature reaching its peak followed by gradual fall in the temperature. Increasing the biodiesel concentration in the ULSD blend (B30 and B60) elevated and delayed the temperature peak along the whole length of the monolith, producing temperatures beyond the most favourable range for the reforming reactions (700°C -900°C) [32]. The diesel has in its composition a high level of aromatics that makes the molecule more stable, and thus, the combustion energy is lower compared to compounds which do not have aromatics in their composition, as the case of biodiesel. In the case of an oxidation reaction, samples with higher biodiesel fraction show more affinity to oxidation process and result in a wider exothermic area and a higher temperature [27]. Also, higher oxygen content of the blends with higher fraction

of biodiesel contributes to increased level of exothermic oxidation reactions taking place on the catalyst bed. As a result, the addition of biodiesel prolonged the oxidation rate rather than the endothermic reforming reactions resulting in a lower catalyst length within the optimal temperature range for the reforming reactions as well as a higher portion of the fuel blend to be oxidised for this specific case.

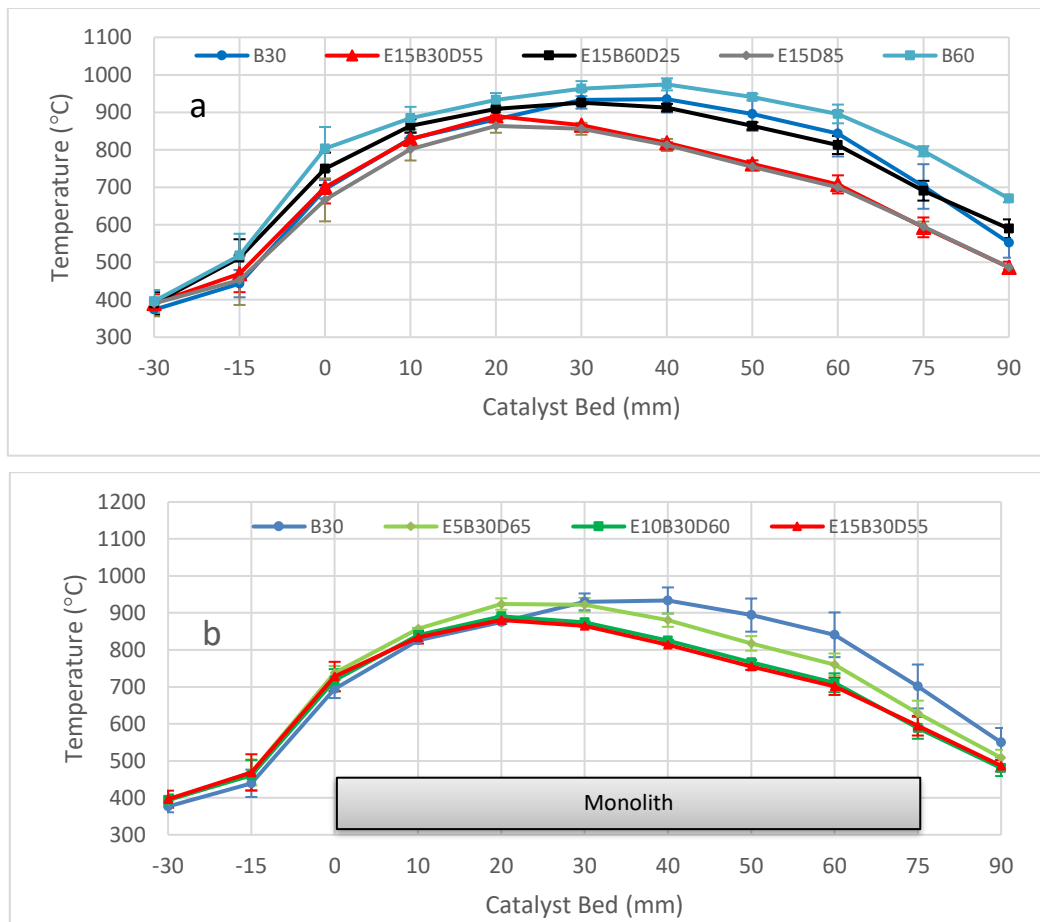


Figure 5. Effect of fuel blends composition (a) and bioethanol concentration (b) on temperature distribution in the reactor for 1.05 O/C molar ratio

A further comparison of the temperatures measured along the monolith catalyst bed while reforming at different bioethanol concentrations ranging from 0 – 15% as in B30, E5B30D65, E10B30D60 and E15B30D55 is shown in Figure 5b.

The fuel flow rates were adjusted to provide equal O/C molar ratio through the reactor. Increase in ethanol concentration in the feed fuel results in temperature drop within the catalyst bed and shifts the temperature peak towards the catalyst entrance, thus ethanol might limit the rate of oxidation reactions within the reactor. Furthermore, there are other properties of ethanol which could help to understand the lower reactor temperatures obtained with ethanol incorporation to the fuel blends, as discussed in the following.

Enthalpy of reaction and heat of vaporisation

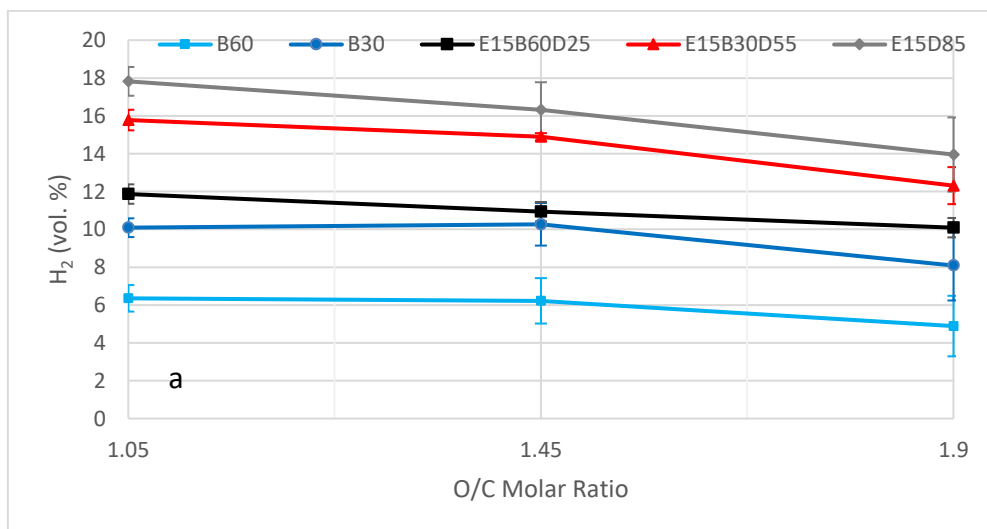
The main reforming reactions of ethanol such as partial oxidation ($\Delta H = +30$ kJ/mol) and steam reforming ($\Delta H = +278.5$ kJ/mol) are both endothermic [33], and also its enthalpy of vaporisation is higher than those of diesel and biodiesel which result in a lower reaction temperature. This lower temperature could be presented as a challenge for gas-phase reforming reactions to take place and produce synthesis gas [34], while in the case of aiming to maximise thermochemical energy recovery from the engine exhaust this will be beneficial. Depending on the ethanol concentration of the fuel blend, this effect could result in a higher proportion of the catalyst length to be within the optimal reforming temperature range for syngas production compared to conventional diesel and biodiesel. This favourable thermal effect of ethanol incorporation occurs for all the three O/C molar ratios studied here, being more beneficial in the case of the highest O/C ratio where the temperatures using conventional diesel and biodiesel are beyond the optimal temperature range. However, there is also the possibility that the reduction in temperature would require the introduction of more external heat or promoting a higher level of ethanol oxidation to maintain syngas production. These approaches will reduce the efficiency of the reforming process as well as reducing the fuel availability for syngas production.

Ethanol water content

The presence of higher water content within the ethanol molecule might favour earlier initiation along the monolith of the endothermic steam reforming, while maintaining the catalyst in active mode and its stability by reducing coking formation [32]. Also, the higher water content in the ethanol compared to both ULSD and biodiesel can promote the water gas shift reaction (WGSR). Fuel blends with very high ethanol content also could decrease catalyst temperature due to the water content of ethanol resulting on the effects on syngas production previously described.

3.3 Effect of fuel blend on the reformat composition

To experimentally study the biodiesel effect on the reforming reactions, the product gas composition of E15B0D85, E15B30D55, E15B60D25, B30, and B60 reforming at various O/C molar ratios are shown in Figure 6. In addition to H_2 and CO , as the main components of the resultant syngas, there are also other species in the reformat such as H_2O , CO_2 , and hydrocarbons derived from combustion, partial oxidation, and thermal decomposition of the fuel blend [24].



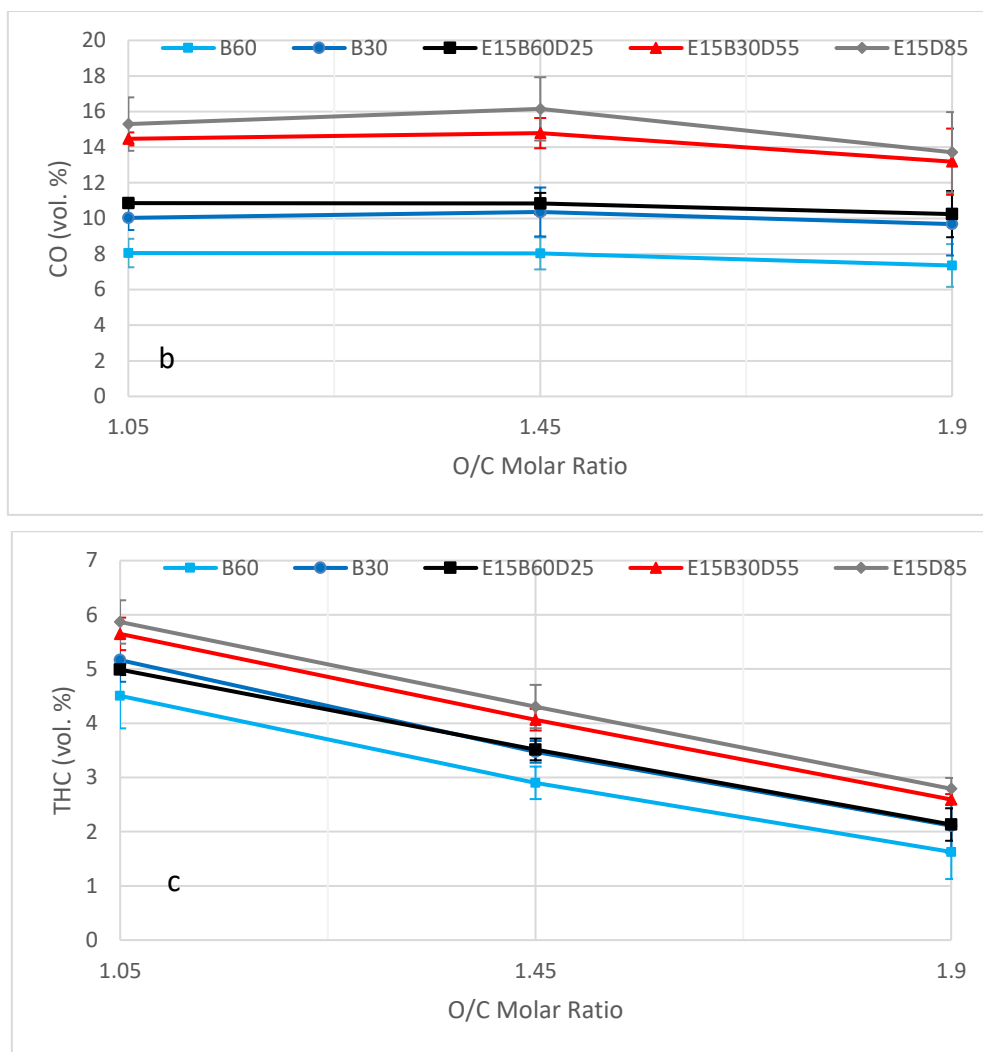


Figure 6. Effect of biodiesel addition on the product gas distribution from reforming of different fuel blends at various O/C molar ratios

The proportions of H_2 , CO, and THC in the reformer product gas decreased with increasing O/C molar ratio due to the oxidation reactions of these products, to form CO_2 and H_2O . With increase in O/C molar ratio, the production of THC in the product gas decreased, but the hydrogen concentration is adversely affected. Therefore, as mentioned earlier O/C molar ratio should be just sufficient to generate enough heat by the exothermic oxidation reactions to reach the adequate catalyst temperature for the reforming reactions to take place. H_2 production decreased with increasing the amount of biodiesel in the fuel blends (Figure 6a). The reforming of fuel blends containing 60% biodiesel shows decreased hydrogen content in the reformer product gas by up to 40% in both the ethanol containing fuel blend and the biodiesel-diesel (BD) blends. The CO content also decreased with increasing the proportion of the biodiesel

(Figure 6b). Similarly, the THC_s in the reactor product gas decreased with increasing biodiesel as shown in Figure 6c. These results imply that adding biodiesel in the blend elevates the oxidation rates resulting in higher temperatures (as previously shown in Figure 5) thus, interfering with the steam reforming reactions [6].

For all the considered fuel blends and the O/C molar ratios the amount of hydrogen (Figure 7a) and CO (Figure 7b) produced in the reactor increased with increasing ethanol content in the studied range (0-15% ethanol). Increasing the ethanol concentration in the fuel blends also results in higher proportion of THC in the reactor product gases, indicating hydrocarbon breakdown and reforming reactions rather than complete oxidation are promoted under the presence of ethanol (Figure 7c). It is noteworthy that increase in ethanol content results in a reduction in the percentage of CO₂ in the products, which might be due to the contribution from dry reforming where CO₂ reacts with the fuel to produce additional CO and H₂.

These results reveal the clear relationship between the ethanol concentration and the reforming performance of the blends to produce syngas. In addition to the thermodynamic properties of ethanol (e.g. enthalpy of reaction, enthalpy of vaporisation, etc.) already explained in the previous section, other potentially influential parameters on the effect of ethanol are discussed in the following.

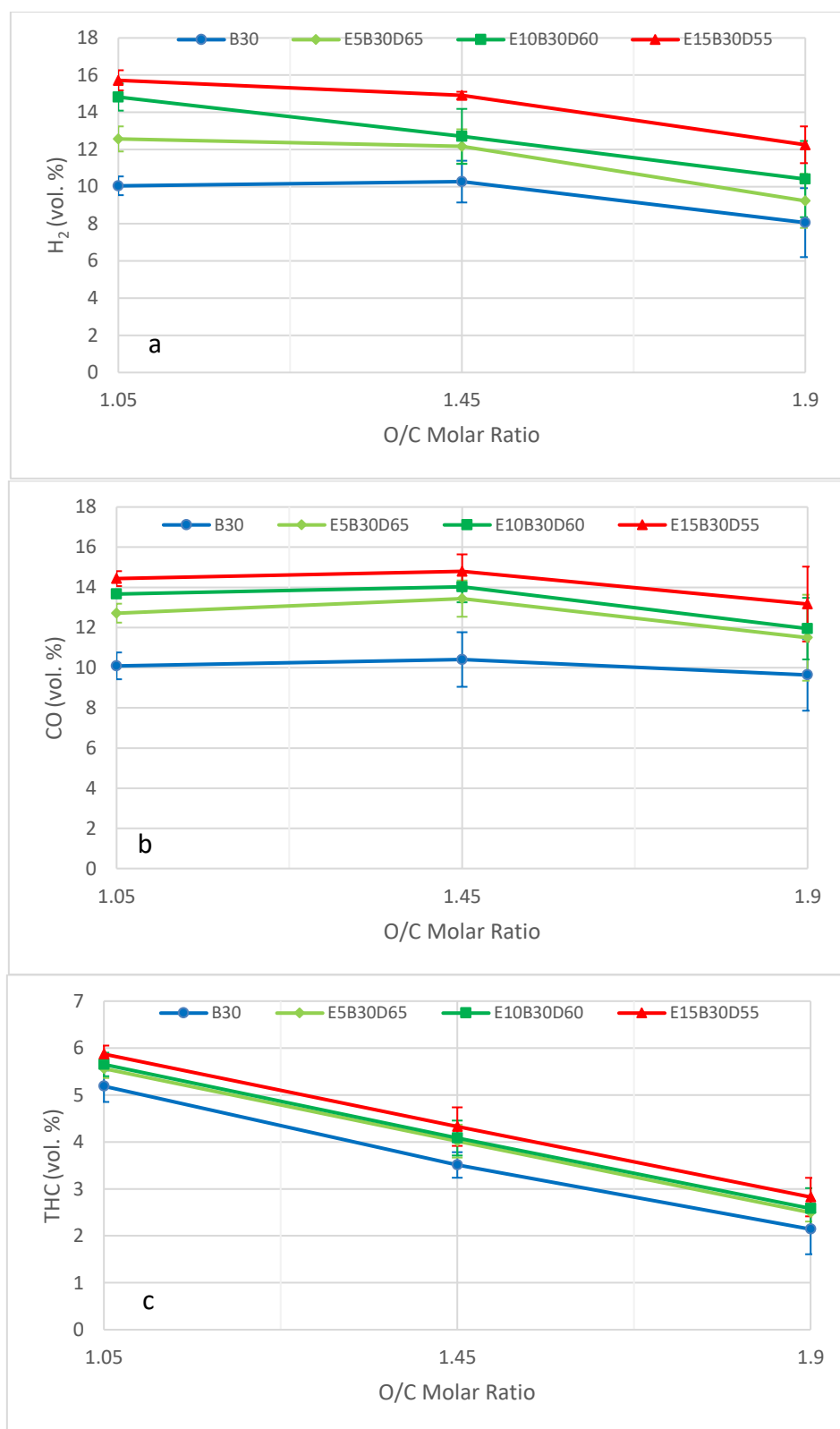


Figure 7. Product gas composition from reforming of various ethanol addition into the fuel blends at B30.

It is reported that light alcohols have unique surface adsorption characteristics and surface reaction pathways which in the presence of the catalyst and adequate temperature could result in high reforming efficiency through both partial oxidation [35] and steam reforming [36]. The high adsorption strength of ethanol in the surface of the catalyst is through the lone pair electrons on the oxygen atom. This is followed by quick dehydrogenation of the atom attached to the oxygen forming ethoxy radical through surface reactions in the catalyst. Those ethoxy radicals form a very reactive oxametallacycle bridge thanks to the presence of rhodium [37] followed by its rapid decomposition and further reactions to produce syngas and other reforming products depending on the reaction conditions in terms of oxygen and water availability, temperature, etc. In contrast to ethanol, in the case of alkanes (which represent around 30% of the composition of the conventional diesel fuel used in this study), their adsorption and activation in the catalyst surface follows different pathways [38] being the limiting step in the reforming reactions [39].

The C/H ratio of the fuel is another parameter that affects the hydrogen production in the reactor. The C/H ratio of ethanol is 0.33 while for conventional diesel is 0.53 and for biodiesel is 0.54, both much higher than that for ethanol. The lower C/H ratio of the ethanol is beneficial in terms of higher hydrogen yield and better resistance to catalyst deactivation. Therefore, for the tests carried out in this study, the increase in ethanol content in the blends decreased the overall C/H ratio of the blend which could be a contributing factor to increase hydrogen production. Furthermore, the lower molecular mass, lower viscosity and shorter chain length of ethanol are factors which give it a higher diffusivity compared to most of the hydrocarbon components present in the conventional diesel fuel and biodiesel. Also, the short chain molecular structure of ethanol can reduce the possibility of catalyst deactivation. It is reported that alcohols with longer chain length reduce hydrogen yield and they can partially deactivate

the catalyst through the formation of olefins and coke which could be strongly adsorbed to the catalyst active sites inhibiting reforming reactions [40].

In addition to the aforementioned parameters, it is extensively reported that the addition of water enhances steam reforming to produce hydrogen [10,12,15,41]. According to Vesselli et al [33] the higher water content of ethanol than diesel and biodiesel could enhance hydrogen production by further promoting steam reforming reaction which is also beneficial in avoiding catalyst coking.

As a conclusion, regarding all the aforementioned ethanol properties (i.e. enthalpy of reaction, enthalpy of vaporisation, reactivity, H/C ratio, diffusivity, steric hindrance, water content, etc.), a quicker and more favourable fuel conversion to syngas is expected for ethanol compared to conventional diesel fuel and biodiesel. Overall, it is deduced that ethanol is reformed earlier than conventional diesel fuel and biodiesel, thus ethanol will have the oxygen available to react further upstream. This could be another reason to justify the higher hydrogen production with ethanol incorporation to the fuel blends. As ethanol consumes the oxygen the actual O/C ratio for conventional diesel and biodiesel will be lower than expected, resulting in lower fuel oxidation and higher hydrogen production.

3.4 Reforming Process efficiency

Reforming efficiency was calculated based on the lower heating value and the mass flow rates of combustible species in the reformat and that of the reformer feed fuel. Based on the definition, two different reforming efficiencies are introduced; the first taking into account only hydrogen and CO in the reformat, and the second considering the total hydrocarbons as well (Eq. ii and Eq. iii).

H₂ & CO Reforming efficiency

$$= \frac{(LHV \times \dot{m}) \text{ Of } H_2 \text{ and CO in the reformat}}{(LHV \times \dot{m}) \text{ of the input fuel}} \quad (i)$$

H₂, CO & THC Reforming efficiency

$$= \frac{(LHV \times \dot{m}) \text{ Of } H_2, \text{ CO and THC in the reformat}}{(LHV \times \dot{m}) \text{ of the input fuel}} \quad (ii)$$

The reforming efficiencies of the blended fuels for O/C ratio of 1.45 are demonstrated in Figure 8.

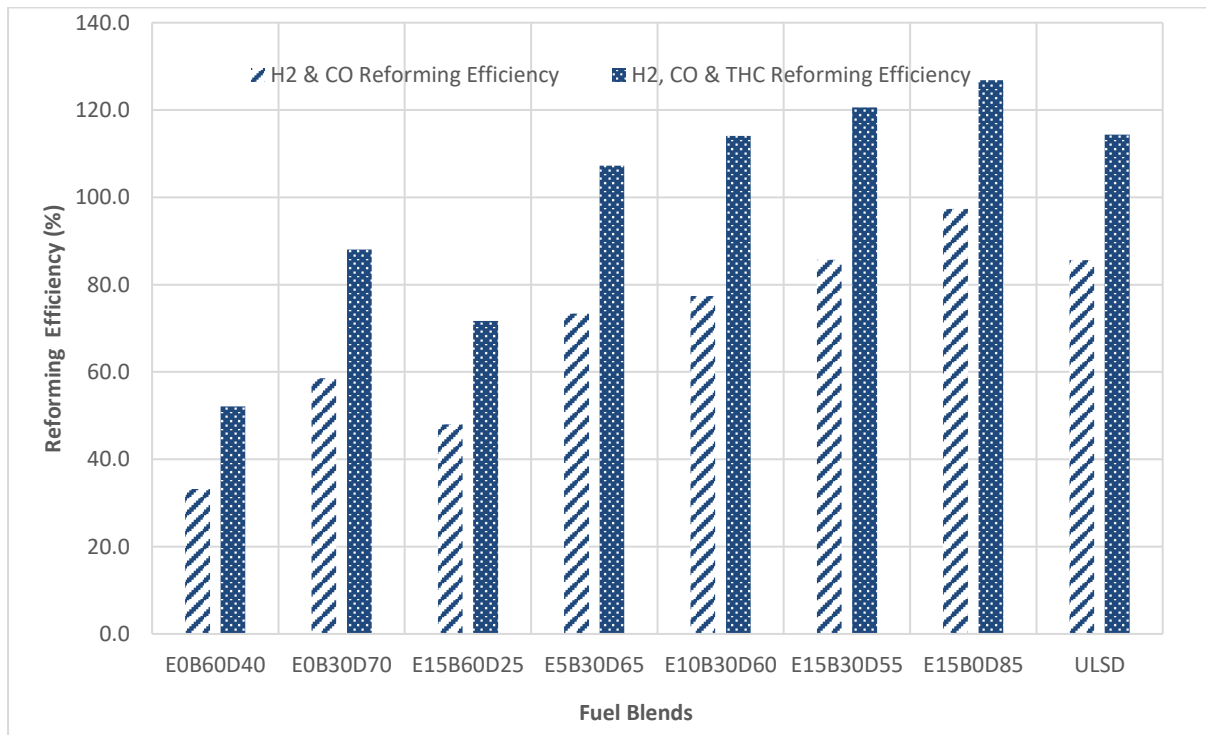


Figure 8. Reforming process efficiency of various ethanol-biodiesel-diesel fuel blends

Results indicate that there are significant differences between the fuel blends in terms of reforming process efficiency. This efficiency drop in B60 is due mainly to the successive oxidation reactions taking place along the catalyst bed, which is in correlation with the previously discussed effects of biodiesel addition to the fuel blend. The oxidation of the feed fuel results in the net reduction in the number of moles of H₂ and CO produced in the reactor

product gas. Considering the previous discussion, it is deduced that to reverse this trend and to improve reforming efficiency, ethanol can be added to the main fuel, i.e. biodiesel–diesel blends, to effectively generate a more hydrogen – rich reformat suitable for the purpose of diesel emissions control. This is because ethanol promotes steam reforming and partial oxidation reactions rather than oxidation, leading to higher yields of H_2 and CO and higher process efficiency.

4. Conclusion

This study investigates the potential of a new capacity of utilizing bioethanol in compression ignition powertrains and improving energy recovery from the exhaust. Exhaust assisted fuel reforming of ethanol-biodiesel-diesel fuel blends is examined as an influential thermochemical recovery method to produce on-board hydrogen with the aim of further lowering the carbon footprint of the diesel powertrains. Although it is demonstrated that the reforming offers improvement in the overall carbon emission for all the studied blends, the effectiveness of the energy recovery and H_2 production is shown to have a strong dependency on physiochemical properties of the individual fuels, as well as the mixture composition and temperature, which control the extent of major reaction mechanisms. Accordingly, it is deduced that the ethanol-rich blends offer a higher recovery efficiency favouring hydrogen and carbon monoxide production, which mainly is attributed to the specific thermochemical properties of ethanol. The investigations conclude that deployment of exhaust assisted fuel reforming of ethanol-biodiesel-diesel blends can potentially offer a noticeable amount of on-board heat recovery. This can lead to a promising fuel replacement and, as an outcome, lower carbon emission levels could be achieved in diesel engines. This, as a practical strategy, can serve as an effective vector in the cumulative challenge towards a greener future road transportation in accordance with the global environmental aspirations.

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