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DOI:

[10.1039/C5RA03111G](https://doi.org/10.1039/C5RA03111G)

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Document Version

Peer reviewed version

Citation for published version (Harvard):

Fennell, D, Herreros, J, Tsolakis, A, Cockle, K, Pignon, J & Millington, P 2015, 'Thermochemical recovery technology for improved modern engine fuel economy - part 1: analysis of a prototype exhaust gas fuel reformer', *RSC Advances*, vol. 5, no. 44, pp. 35252-35261. <https://doi.org/10.1039/C5RA03111G>

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1 **Thermochemical recovery technology for improved modern engine fuel economy - Part 1: Analysis of**
2 **a prototype exhaust gas fuel reformer**

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8
9
10 **Abstract**

11 Exhaust Gas Fuel Reforming has the potential to improve the thermal efficiency of internal combustion
12 engines, as well as simultaneously reduce gaseous and particulate emissions. This thermochemical
13 energy recovery technique aims to reclaim exhaust energy from the high temperature engine exhaust
14 stream to drive catalytic endothermic fuel reforming reactions; these convert hydrocarbon fuel to
15 hydrogen-rich reformat. The reformat is recycled back to the engine as Reformed Exhaust Gas
16 Recirculation (REGR), which provides a source of hydrogen to enhance the engine combustion process
17 and enable high levels of charge dilution; this process is especially promising for modern gasoline direct
18 injection (GDI) engines.

19 This paper presents a full-scale prototype gasoline reformer integrated with a multi-cylinder GDI
20 engine. Performance is assessed in terms of the reformat composition, the temperature distribution
21 across the catalyst, the reforming process (fuel conversion) efficiency and the amount of exhaust heat
22 recovery achieved.

23 **Keywords**

24 Exhaust-gas fuel reforming; hydrogen; reformat; Reformed Exhaust Gas Recirculation (REGR); energy
25 recovery

26 **Abbreviations**

27	TDC	Top Dead Centre
28	CO	Carbon Monoxide
29	EGR	Exhaust Gas Recirculation
30	EGT	Exhaust Gas Temperature
31	FTIR	Fourier transform infra-red detector
32	GC-FID	Gas chromatograph with flame ionisation detector
33	GC-TCD	Gas chromatograph with thermal conductivity detector
34	GDI	Gasoline Direct Injection
35	GHSV	Gas hourly space velocity
36	HC	Hydrocarbon
37	IMEP	Indicated Mean Effective Pressure
38	LHV	Lower heating value
39	NO _x	Oxides of Nitrogen
40	PM	Particulate Matter
41	REGR	Reformed Exhaust Gas Recirculation
42	TWC	Three Way Catalyst

44 **1. Introduction**

45 Exhaust gas fuel reforming is a technique with potential to achieve energy recovery from the exhaust
 46 stream of internal combustion engines in order to raise the engine thermal efficiency and reduce fuel
 47 consumption, as well as reduce exhaust emissions¹⁻³. The feasibility of this thermochemical energy
 48 recovery process relies on ensuring that the overall process is endothermic and energy is captured from
 49 the exhaust stream. The major reforming reactions are listed in Table 1. The two primary chemical
 50 reactions, steam reforming (1) and dry reforming (2) are endothermic and reform hydrocarbon (HC)
 51 fuel into hydrogen and carbon monoxide with a net gain in fuel enthalpy. Carbon dioxide and steam are
 52 supplied as reactants by the engine exhaust gas, and the hydrogen-rich product gases are re-circulated
 53 to the intake system for in-cylinder combustion, completing the reformed exhaust gas recirculation
 54 (REGR) system.

55 If oxygen is present in the exhaust gas then some fuel will be consumed by highly exothermic oxidation
 56 reactions. Previous exhaust gas fuel reforming studies⁴ have revealed that the combustion reaction (3)
 57 prevails but some partial oxidation (4) is also possible. In some applications the oxidation reactions are
 58 used to increase the catalyst temperature in order to improve the hydrogen yield, for instance by
 59 Partial Oxidation reformers and Autothermal reformers. The less exothermic water-gas shift (WGS)
 60 reaction (5) also increases the hydrogen concentration by reacting CO, which has already been
 61 produced by the other reforming reactions, with steam. The process efficiency is reduced to some
 62 degree by these exothermic reactions.

63 Table 1 – General formulae for the key reforming reactions in hydrocarbon fuel reforming

Reaction	General chemical formula	* Enthalpy of reaction, MJ/kmol
Steam reforming:	$C_xH_y + xH_2O \rightarrow xCO + (x + \frac{y}{2})H_2$	$\Delta h_R = (+ 1259)$ (1)
Dry reforming:	$C_xH_y + xCO_2 \rightarrow 2xCO + \frac{y}{2}H_2$	$\Delta h_R = (+ 1588)$ (2)
Combustion:	$C_xH_y + (x + \frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$	$\Delta h_R = (- 5116)$ (3)
Partial oxidation:	$C_xH_y + \frac{x}{2}O_2 \rightarrow xCO + \frac{y}{2}H_2$	$\Delta h_R = (- 676)$ (4)
Water-gas shift:	$CO + H_2O \rightleftharpoons CO_2 + H_2$	$\Delta h_R = (- 283)$ (5)

64 * when calculating enthalpy of reaction it was assumed that: HC fuel is *n*-octane; reactions go to completion;
 65 products and reactants are at 25°C and 1 atm; and water is in the gaseous state. Thermodynamic data from⁵
 66

67 Other classifications of reformer have been researched for on-board hydrogen generation in the past.
 68 Partial oxidation reformers⁵⁻⁷ react air and HC fuel to produce reformat, which, when coupled with a
 69 gasoline engine, can extend the (air or EGR) dilution limit and improve engine efficiency and emissions.
 70 These systems can be useful for cold engine starts operating partially or solely on reformat in order to

71 reduce emissions during warm-up^{6, 7}. However, the engine-reformer system efficiency ultimately
72 suffers due to energy lost in the exothermic partial oxidation reforming process. A plasma reformer^{8,9}
73 instead uses electrical power to convert HC fuels to reformat. Again, the overall engine-reformer
74 system efficiency is reduced due to the electrical power required for the reforming process. None of
75 these systems aim to achieve exhaust heat recovery.

76 Ethanol reformers designed to achieve heat recovery from ethanol-fuelled¹⁰ and gasoline-fuelled¹¹ SI
77 engines have been developed more recently. Ethanol can be reformed more easily than the longer
78 chain and more complex (e.g. aromatic) HC components of gasoline and so it is possible at lower
79 temperature, typically between 300-350 °C¹⁰. This makes ethanol reforming feasible over most of the
80 operating range of a SI engine.

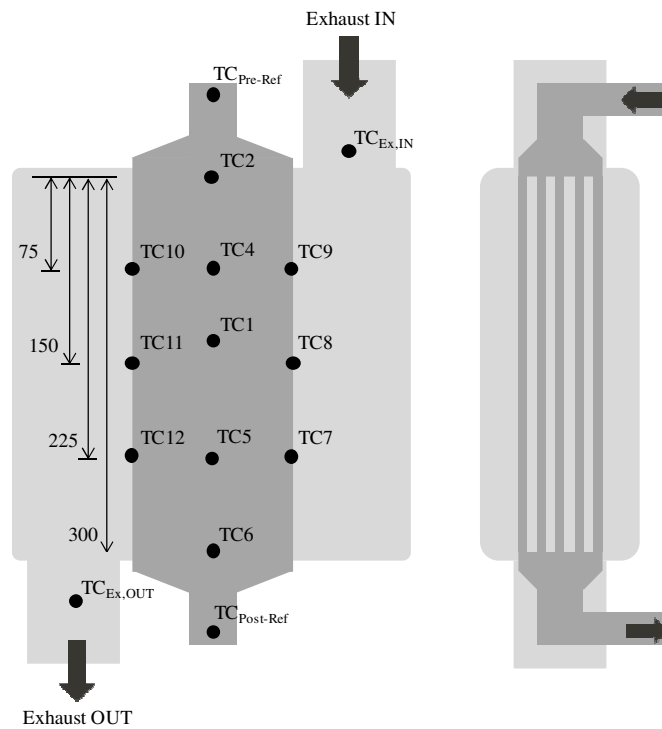
81 The gasoline reformer has potential for more widespread use than ethanol and E85 but greater
82 technical barriers to overcome, most notably with respect to achieving effective performance at
83 sufficiently low temperature to be feasible with the gasoline engine exhaust stream. Because reformer
84 performance is heavily dependent upon catalyst temperature, reformer design should be focussed to
85 ensure efficient heat transfer from the exhaust stream and minimise heat losses^{4,12}.

86 Exhaust gas fuel reforming has great potential for improving engine efficiency and reducing exhaust
87 emissions. A review article by Golunski¹³ discussed the application of exhaust gas fuel reforming for
88 improving the thermal efficiency of IC engines through enhanced combustion and novel after-
89 treatment solutions. Thermodynamic and experimental studies of the REGR reactions have shown that
90 precious metal catalysts, e.g. Rhodium on Zirconia^{14, 15}, exhibit high activity with yields close to
91 equilibrium at temperatures typical of the gasoline engine exhaust. A recent experimental study¹ using
92 hydrogen and CO addition to conventional EGR highlights the potential benefits that REGR can offer to
93 the GDI engine, with simultaneous reductions in NO_x, PM and CO, only slightly increased HCs, and
94 increased engine and total system thermal efficiency.

95 This paper furthers the research in the field of exhaust gas fuel reforming as, for the first time, a full-
96 scale gasoline reformer integrated with a modern production multi-cylinder GDI engine was studied.
97 The results discussed in this paper are focussed on the prototype reformer performance; this includes
98 examination of the reformer temperature profiles, analysis of the reformat composition including HC
99 speciation, and calculation of the reformer fuel conversion efficiency. Devices designed to achieve
100 exhaust heat recovery may be subjected to exergy analysis, and this has been applied here to establish
101 the influence of exhaust gas fuel reforming on the exergy, or 'available energy', of the exhaust stream.
102 The efficiency and emissions performance of the GDI engine utilising exhaust gas fuel reforming will be
103 presented in a follow-up paper.

104 **2. Experimental setup and test conditions**

105 The reformer and catalyst were designed by Johnson Matthey and it consists of a stack of five metallic
106 catalyst plates (8.8in³ each) coated with 3.6g/in³ of ceramic support (Ceria-Zirconia-Alumina) loaded
107 with 3.3% Platinum - 1.7% Rhodium. Rhodium offers very good sulphur tolerance, excellent thermal
108 stability and resistance to coking, and stable catalyst performance was experienced throughout the 6
109 month test program. Each catalyst plate is mounted between two finned stainless steel plates used to
110 seal it from the exhaust stream. The reformer plate assembly was designed to ensure high heat transfer
111 from the hot exhaust gas to the catalyst, using fins on the stainless steel surround for increased surface
112 area and a narrow catalyst construction only four cells thick. The exhaust stream flows over the
113 reformer plate stack, which is positioned after the TWC. The reformer feed gas is extracted from the
114 exhaust stream before the TWC, mixed with gasoline, and routed around the outer skin of the TWC to
115 assist with fuel vaporisation and feed gas pre-heating. The required flow rate of gasoline was injected
116 into the reformer feed gas by varying the pulse-width of a solenoid fuel injector, typically used in port
117 injection engines, operating at a fixed frequency of 30Hz. The injector was mounted to the reformer
118 with a manifold cooled by engine water to protect the injector from high exhaust system temperatures.
119 11 thermocouples were distributed over the middle reformer plate according to schematic Figure 1,
120 with additional thermocouples in the feed gas, product gas, and exhaust stream before and after
121 passing over the reformer assembly.



122 Figure 1 - Reformer schematic indicating thermocouples (TC) locations on the central reformer plate
123 and in the exhaust stream
124

125 *Reformer installation:* The reformer was installed with a turbocharged 2L GDI engine, positioned in the
 126 exhaust stream after the TWC. The REGR system installation used a ‘high pressure’ recirculation
 127 configuration, inducting reformat directly into the intake manifold. The system consisted of an
 128 integrated DC motor controlled EGR valve and cooler, and an additional cooler, all supplied with engine
 129 coolant to maintain acceptable gas and component temperatures.

130 *Reformat analysis:* A MKS Instruments Multigas 2030 Fourier Transform Infra-Red (FTIR) spectrometer
 131 was used to analyse the reformat stream for multiple species, including CO₂, CO, H₂O, NH₃ and a
 132 selection of hydrocarbons compounds including methane. A HP 5890 Series 2 gas chromatograph with
 133 thermal conductivity detector (GC-TCD) and HP 3395 integrator was used to measure the hydrogen
 134 concentration in the reformat stream. Argon at 40psi acted as the carrier gas to the sample fed at
 135 10psi, resulting in the hydrogen peak occurring at 2.4s retention time. The detector was calibrated with
 136 10% and 30% hydrogen in nitrogen. Another HP 5890 Series 2 gas chromatograph with flame ionisation
 137 detector (GC-FID) gave in-depth speciation of the HC components of the reformat. The GC-FID was
 138 calibrated with 15 common HCs ranging from C1 to C7 (Table 2).

139 Table 2 – Hydrocarbon species included in GC-FID calibration

HC species	Formula	HC species	Formula	HC species	Formula
Methane	CH ₄	1 - butane	C ₄ H ₁₀	n-pentane	C ₅ H ₁₂
Ethylene	C ₂ H ₄	1,3-Butadiene	C ₄ H ₆	n-hexane	C ₆ H ₁₄
Propylene	C ₃ H ₆	n-butane	C ₄ H ₁₀	Benzene	C ₆ H ₆
Propane	C ₃ H ₈	3-Methyl-1-butene	C ₅ H ₈	n-heptane	C ₇ H ₁₆
Iso-butane	C ₄ H ₁₀	Iso-pentane	C ₅ H ₁₂	Toluene	C ₇ H ₈

140 A Horiba MEXA-7100DEGR measured the intake manifold and exhaust stream CO₂ concentration in
 141 order to calculate the charge dilution rate according to equation (6). The FID component of the Horiba
 142 analyser was also useful for providing a measurement of the total HC content of the reformat, which
 143 was not possible with the FTIR analyser.

$$Charge\ Dilution\ Rate, \% = \frac{(CO_2)_{manifold}}{(CO_2)_{exhaust}} \times 100 \quad (6)$$

144 *Test conditions:* Three engine conditions were selected in order to generate a suitable range of
 145 reformer temperature and flow conditions; these were 35Nm/3bar IMEP at 2100rpm, 50Nm/4bar IMEP
 146 at 3000rpm, and 105Nm/7.2bar IMEP at 2100rpm. The first two conditions are key steady state
 147 conditions used on the new European drive cycle for a mid-size/large family vehicle with a 2 litre
 148 engine, and the third condition is typical of a higher load transient condition. At each condition the
 149 engine was operated with the maximum achievable charge dilution rate, and also a lower dilution rate
 150 to investigate the effect of reformer mass flow rate, or gas hourly space velocity (GHSV). Gasoline was
 151 injected into the reformer feed gas such that the molar concentration was 0.5% and 1% (fuel

152 composition assumed to be octane) to test the influence of fuel concentration on reformer
 153 performance. Excess fuel can result in a reversible catalyst deactivation by coke lay down. The fuel
 154 addition was optimised to avoid this fouling while maintaining good H₂ production and the test
 155 procedure involved periodically operating with EGR to expose the catalyst to steam and oxygen in order
 156 to reverse any coking that may have occurred.

157 The engine-out exhaust gas composition (Table 3) varied little across the range of conditions tested
 158 because the engine uses a homogeneous, stoichiometric combustion strategy. This can also be
 159 considered the reformer feed gas composition (prior to gasoline injection). The slight variations of the
 160 primary exhaust gas species at each engine condition are due to the use of different charge dilution
 161 rates which influenced the combustion. This also results in larger percentage variation of NO_x and THCs
 162 due to the effects of REGR on the combustion process. The oxygen content of the exhaust stream varies
 163 only between 0.5 to 0.7%, which is of particular relevance to the reformer process efficiency as the
 164 oxygen concentration is directly proportional to the amount of fuel that is oxidised in the reformer and
 165 the resulting increase in temperature.

166 Table 3 - Exhaust gas temperature (EGT) and composition at each engine condition

Engine condition	EGT, °C (Pre-reformer)	CO ₂ , %	O ₂ , %	CO, %	* H ₂ O, %	NO _x , ppm	THC, ppm
35Nm/ 2100rpm	595 - 605	14.8 - 15.0	0.60 - 0.70	0.50 - 0.60	14.3- 14.4	100 - 1200	1900 - 3000
50Nm/ 3000rpm	655 - 680	14.8 - 14.9	0.50 - 0.65	0.50 - 0.55	14.3- 14.4	200 - 600	1500 - 1900
105Nm/ 2100rpm	685 - 720	14.8 - 15.0	0.60 - 0.65	0.55 - 0.70	14.4- 14.5	900 - 2300	1300 - 1600

* Calculated

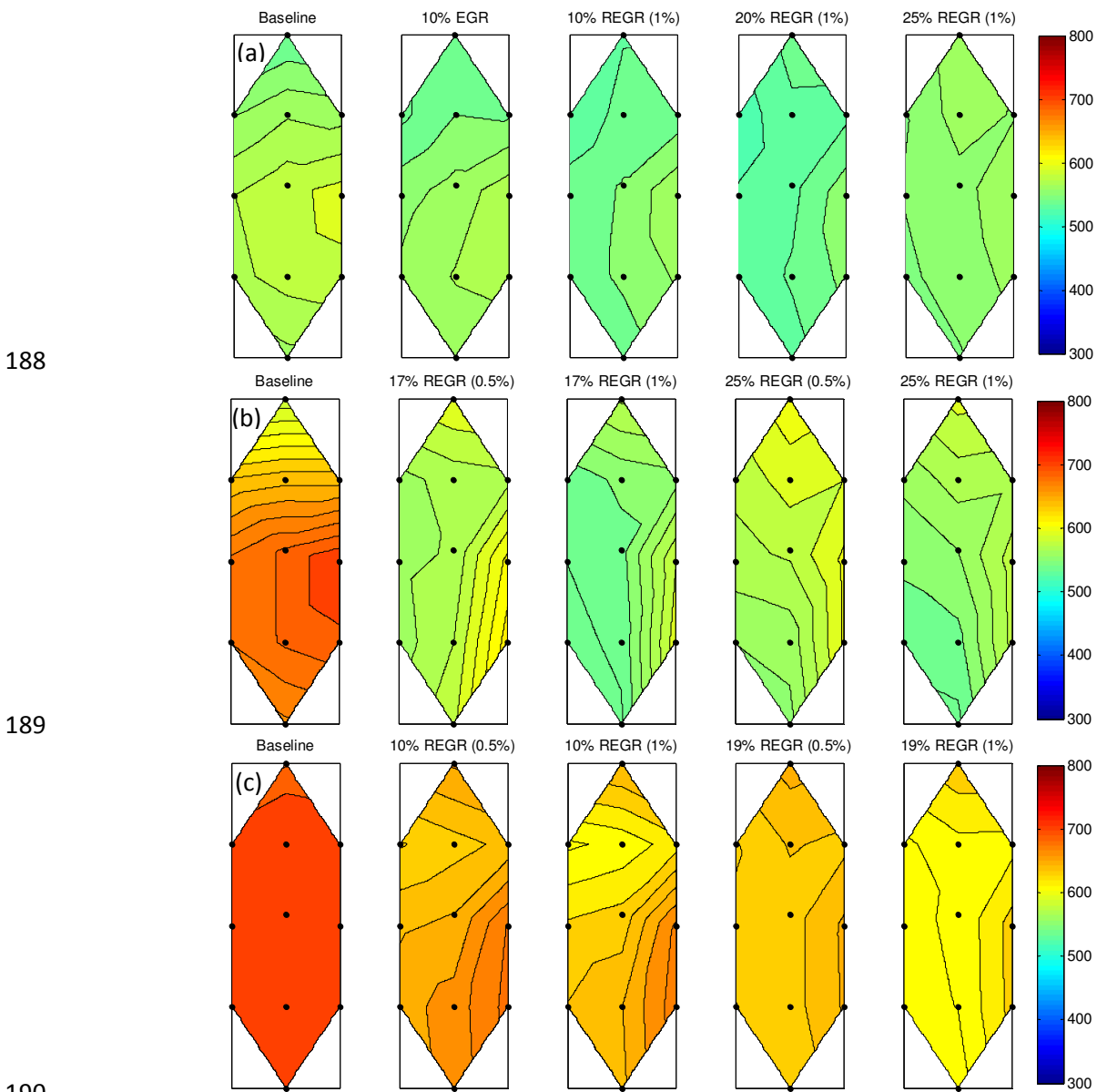
167 3. Results and discussion

168 3.1. Reformate characteristics

169 *Temperature distribution:* The temperature distribution across the middle reformer plate varies with
 170 engine condition, REGR flow rate, fuel concentration, and the resulting reforming activity (Figure 2). In
 171 these plots the reformer feed gas flows from top to bottom and the engine exhaust stream flows over
 172 the plate from right to left. The temperatures were generally higher along the right edge due to the
 173 exhaust stream heating. The baseline plots clearly show that the reformer plates are more effectively
 174 heated as the exhaust stream temperature increases with engine load.

175 At the lowest temperature condition (35Nm/2100rpm) the plate temperatures drop as the REGR flow is
 176 increased up to 20% due to reforming activity. There is also a slight cooling effect just by flowing gas
 177 through the reformer (i.e. with EGR), analogous to a forced-convection cooling process. At the highest
 178 REGR flow rate there is a slight increase in reformer temperature with a more even distribution. This is

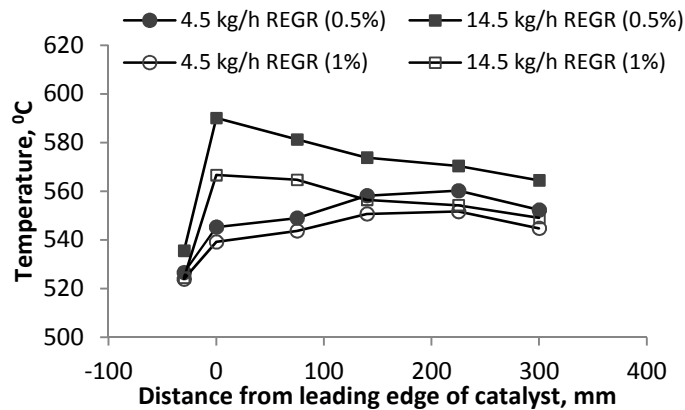
179 the result of multiple effects associated with increasing the flow rate: more oxygen is available for fuel
 180 oxidation which increases the gas temperature in the front of the reformer; the high flow rate moves
 181 the high temperature gas along the reformer more quickly resulting in the more even distribution; and
 182 reforming activity tends to be lower as the flow rate increases.
 183 At the two higher engine load conditions the reformer is heated to significantly higher temperature
 184 when there is no REGR flow (baseline condition). Increasing either the REGR flow or the fuel
 185 concentration lowers the reformer temperature. Both of these changes increase the availability of fuel
 186 while, importantly, at sufficiently high temperature for the endothermic reforming reactions to be
 187 feasible. Again, increasing the REGR flow rate results in a more even temperature distribution.



191 Figure 2 – Temperature (°C) distribution across the middle reformer plate at a) 35Nm, b) 50Nm and c)
 192 105Nm engine conditions, for a range of REGR concentrations (vol.) in the intake charge with either
 193 0.5% or 1% (vol.) gasoline in the reformer feed gas

194

195 *Linear reformer temperature profiles:* Figure 3 compares the linear reformer temperature profiles while
 196 reforming with two different mass flows, 4.5 and 14.5kg/h - this equates to 10% and 25% REGR in terms
 197 of the dilution rate at the 35Nm/2100rpm engine condition. Temperature profiles are included for 0.5%
 198 and 1% fuel in the reformer feed gas. At low reactant mass flow rate in the reformer, there was very
 199 little heating due to exothermic reactions in the front of the catalyst. There was no indication of
 200 endothermic reforming cooling the reformer. It appears that a small amount of reforming occurred in
 201 the first 75mm of the reformer as the temperature remains approximately constant. After this the
 202 temperature increased due to heating by the main engine exhaust stream. At the higher reactant flow
 203 rate there was a greater quantity of fuel and oxygen passing through the reformer which led to a larger
 204 temperature increase at the front face. The combination of higher temperature and more fuel being
 205 available for reforming meant that there was a clear drop in temperature along the length of the
 206 reformer due to endothermic reforming reactions.



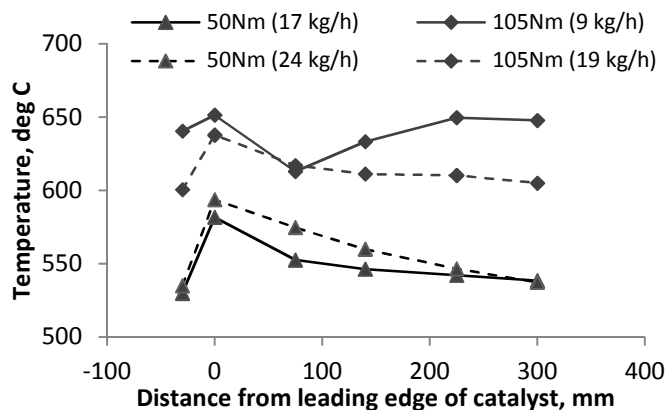
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Figure 3 – Linear reformer temperature profile at the low temperature (35Nm/2100rpm) condition.

209 Increasing the fuel concentration in the feed gas (for a given reactant flow rate) results in a reasonably
 210 uniform reduction of the temperature along the reformer. The feed gas temperature (-30mm from
 211 leading edge) was slightly lower for the higher fuel flow conditions due to greater cooling by fuel
 212 vaporisation, and the gradient of the rise in temperature between the feed gas (-30mm) and the
 213 leading edge (0mm) was similar when comparing each fuel concentration condition. The amount of
 214 oxygen available for oxidation is dependent on the reactant flow rate and determines the amount of
 215 heating at leading edge. The slight reduction of heating with increasing fuel concentration is likely due
 216 to the higher rate of endothermic reforming (decrease in the oxygen/carbon ratio) and slightly higher
 217 specific heat capacity of the feed gas.

218 The effect of reactant mass flow rate in the reformer on the linear temperature profile is shown in
 219 Figure 4 for two engine loads with 1% feed gas fuel concentration in each case. This shows the location
 220 of endothermic reforming moving further along the reformer with increasing flow rate. The initial drop
 221 in temperature is greater for the lower flow condition at each load.

222 When the reformer flow is low and the reformer plate temperature is relatively high at the inlet, 650°C
 223 at the 105Nm condition, most of the reforming occurs in the first section of the reformer and is
 224 followed by re-heating. This implies that the reformer is able to process more fuel than is being
 225 supplied at the low flow condition.



226
 227 Figure 4 - Linear reformer plate temperature profiles for high and low REGR flows at two engine
 228 conditions (1% feed gas fuel concentration in each case)

229 Comparing the two curves for the high temperature condition (105Nm) there is a large temperature
 230 difference in the final 100mm of the reformer. The conditions in this section can be used to give an
 231 insight into the equilibrium position of the WGS reaction. The reformer temperature is reduced for the
 232 higher REGR rate which increases the WGS reaction equilibrium constant, resulting in an equilibrium
 233 shift towards higher H₂ and CO₂ concentration by consuming CO and H₂O. For this reason, increasing
 234 the REGR rate generally results in a greater hydrogen/CO ratio (providing conditions are reasonable for
 235 reforming) this can be seen by comparing the hydrogen and CO data in Figure 55, particularly for the 1%
 236 feed gas fuel concentration conditions.

237 It should be emphasised that the linear profiles offer a 1-dimensional view of the reformer operating
 238 temperature. This information disregards the temperature distribution across each reformer plate and
 239 any difference between the five individual plates.

240 *Reformate speciation:* Maximum hydrogen production was observed when the consumption of steam
 241 was greatest, which indicates successful promotion of the steam reforming reaction (Fig. 5). This
 242 occurred at the 50Nm/3000rpm engine condition, when there was 11% hydrogen produced and 6% un-
 243 reacted steam measured in the reformate, and there was a combination of high temperature and
 244 intermediate reactant flow rate. Some CO₂ can be expected to be produced by oxidation and WGS
 245 reactions, and may be consumed by the dry reforming reaction. The CO₂ concentration in the
 246 reformate was relatively consistent at most test points but was reduced slightly for low REGR mass flow
 247 rates. It should be noted that for a given engine load, at lower REGR mass flows the reformer plate
 248 temperatures are higher. This means the reversible WGS reaction has a smaller equilibrium constant, is

249 therefore less favourable towards the reaction products, and so less hydrogen and CO₂ are produced by
250 this reaction.

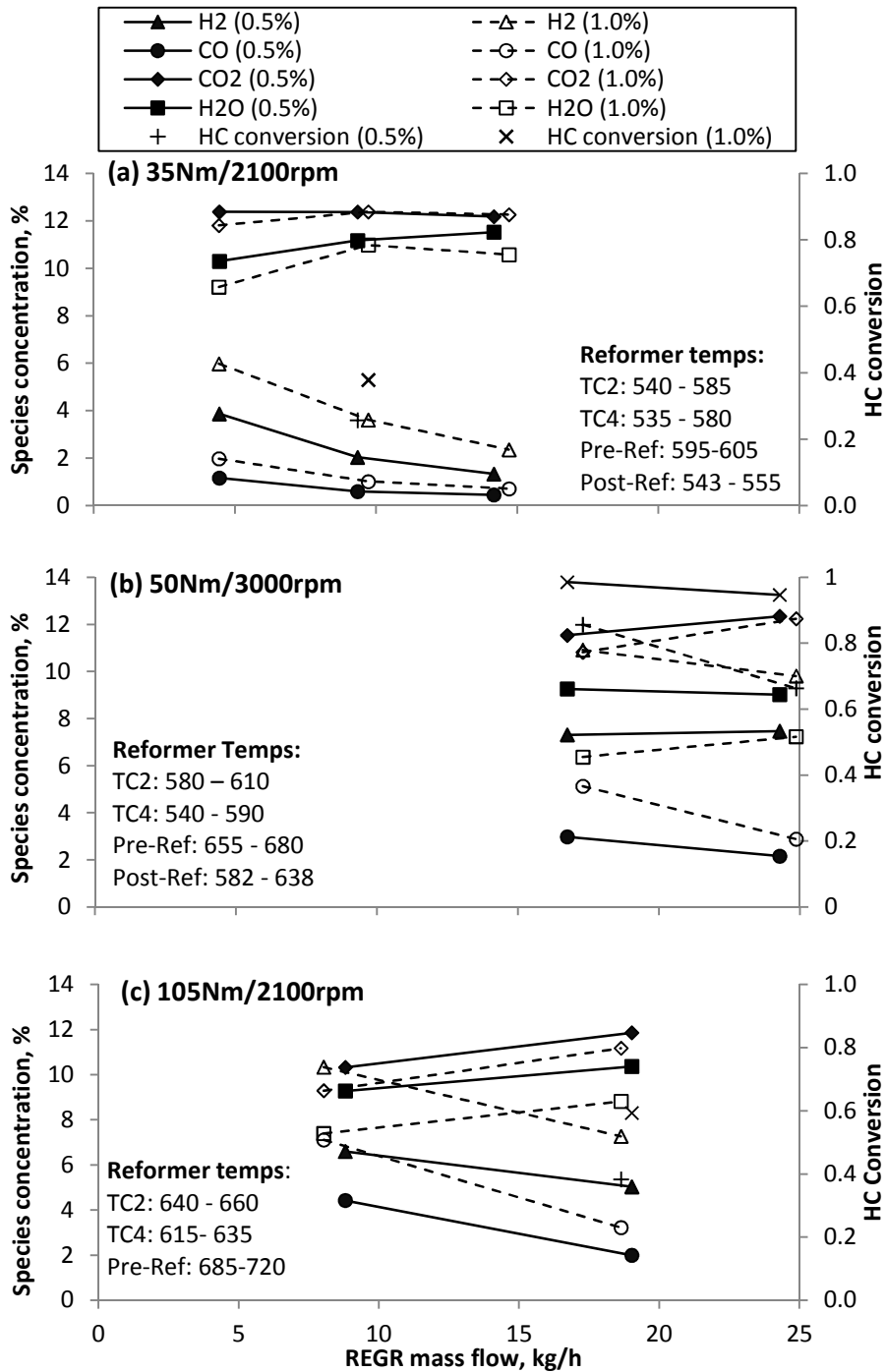


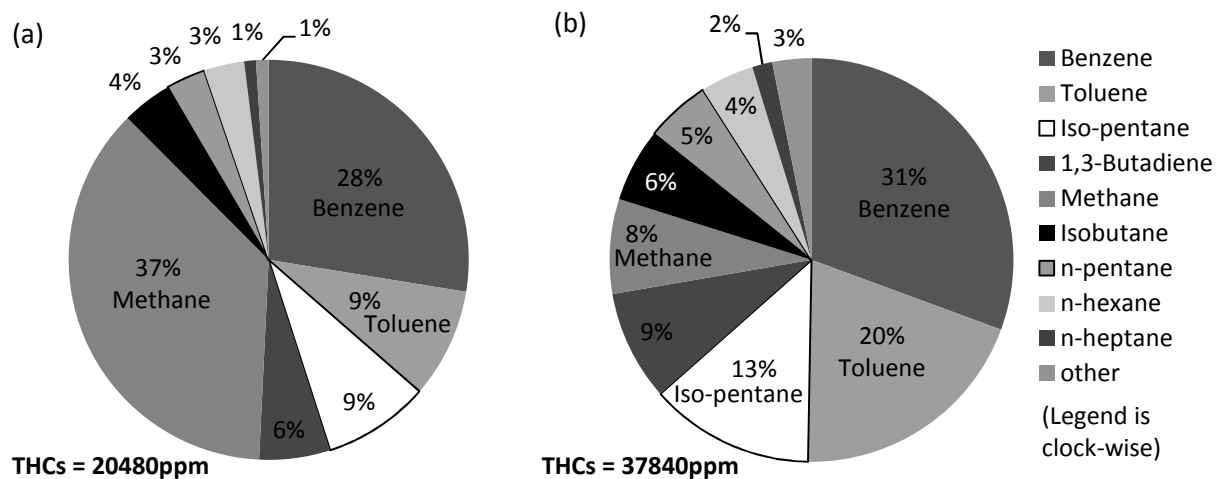
Figure 5 - Reformate species concentrations at various engine conditions (a) 35Nm, (b) 50Nm and (c) 105Nm

251
 252 *Hydrocarbon speciation:* The proportion of HCs that breakthrough the reformer increases with REGR
 253 flow rate; therefore at 17kg/h REGR (Figure 6a) there is a lower total HC (THC) concentration. The
 254 calibration gas used contains many of the major components (Table 2) of gasoline and there were no
 255 significant peaks in the chromatogram spectrum unaccounted for.

256 Methane made up a greater proportion of the HCs in the reformate at lower REGR flow, partly because
 257 the total breakthrough HC quantity was lower, but also due to higher methane production by the

258 'methanation' reforming side reactions; these consume hydrogen in reactions with CO, CO₂ or HCs to
 259 produce methane, but tend to be relatively unfavoured under REGR conditions ¹⁴. The higher
 260 concentration of H₂ and CO produced by the primary reforming reactions at lower REGR flow will lead
 261 to the methanation reactions being increasingly favoured.

262 The molar composition of the gasoline was 12.6% paraffins, 33.4% isoparaffins, 14.6% olefins, 5.1%
 263 naphthenes, 28.9% aromatics and 4.9% oxygenates. The measured aromatic fraction (benzene +
 264 toluene) was higher in each case at 37% and 51%. This supports the idea that the aromatic fraction of
 265 the gasoline is not being reformed as readily as the less complex HCs such as the paraffins, which
 266 constitute nearly half of the gasoline mixture and appear in significantly lower quantity in the
 267 reformat. There is also a smaller toluene/benzene ratio at low reactant flow which implies toluene is
 268 reformed more readily than benzene. It may be that some toluene is partially reformed to the more
 269 stable/less reactive benzene.



270 Figure 6 - Proportion of HC species of the total HCs in reformat as measured by GC-FID at
 271 50Nm/3000rpm with REGR (1% fuel): 17 kg/h (a) and 24 kg/h (b)

272 3.2 Reformer process efficiency

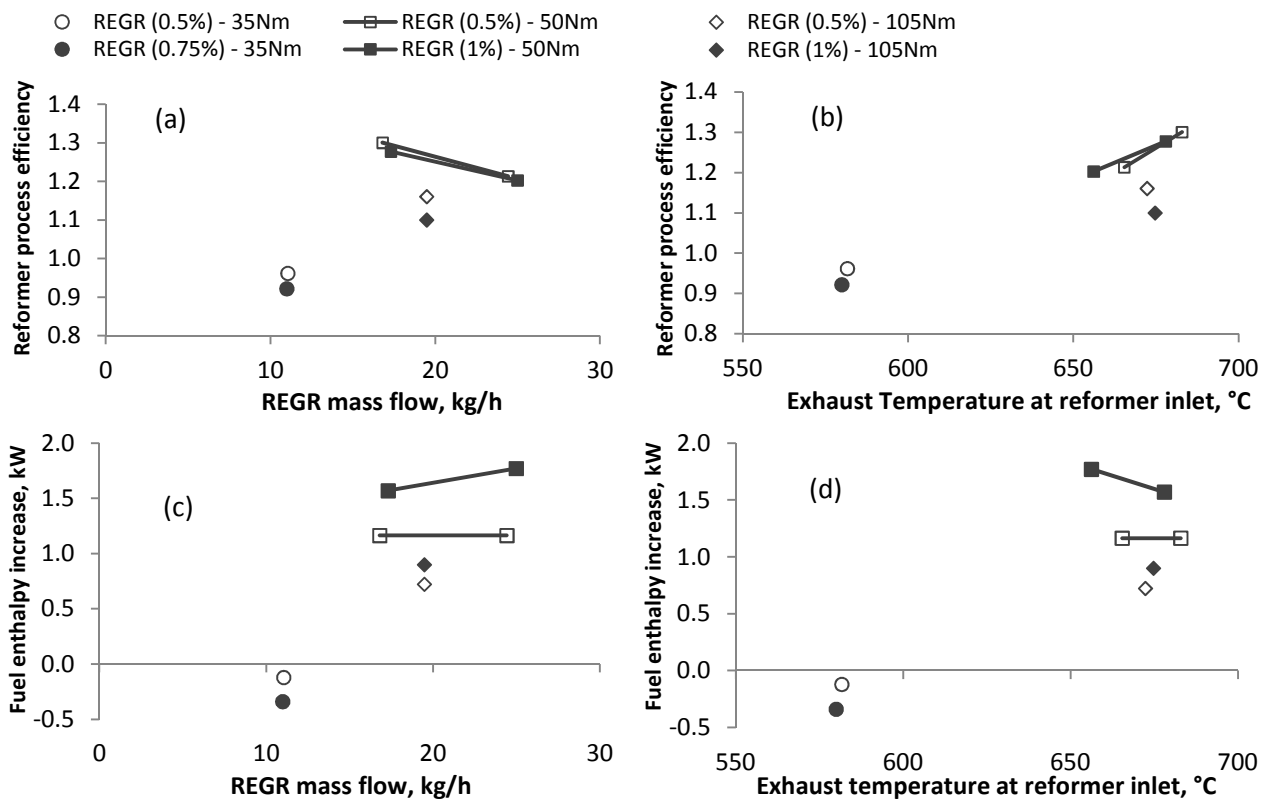
273 The effectiveness of the reformer can be analysed by calculating the reformer process efficiency using
 274 Equation (7). In this equation the HCs and CO contained in the engine exhaust gas which is fed in the
 275 reformer are not included in the calculation of the reformer efficiency. However, they are supplied to
 276 the reformer as products of incomplete in-cylinder combustion, and would usually be considered
 277 wasted energy as the exhaust heat, being both uncombusted species and exhaust heat being used in
 278 the reformer. Therefore equation 7 calculates reformer process efficiency without including those
 279 species as an input energy, contributing in the increase of the reforming process efficiency (Figure 7).
 280 'Dry' measurements were converted to 'wet' molar fractions (using knowledge of the steam
 281 concentration in the feed gas/reformat) before calculating the mass flow rate of individual species.

$$\text{Reformer process efficiency, } \eta_{ref} = \frac{LHV_{H_2} \cdot \dot{m}_{H_2} + LHV_{CO} \cdot \dot{m}_{CO} + LHV_{CH_4} \cdot \dot{m}_{CH_4} + LHV_g \cdot \dot{m}_{HC,out}}{LHV_g \cdot \dot{m}_{g,in}} \quad (7)$$

282

283 At the two highest engine load conditions, when exhaust temperature is above 650°C, the reformer
 284 process efficiency is greater than one (Figure 7a and b). This means that the overall reforming reaction
 285 is an endothermic process leading in the increase of the total fuel enthalpy (Figure 7c and d). The
 286 reformer process efficiency is similar when comparing fuel concentration at each test point; increasing
 287 the fuel concentration to 1% improves further the fuel enthalpy. At the low temperature condition the
 288 reformer process efficiency is less than 1, meaning some energy is lost during the gasoline reforming
 289 process.

290



291 Figure 7 - Reformer process efficiency (a & b) and Fuel enthalpy increase (c & d) plotted against REGR
 292 mass flow (a & c) and exhaust temperature at the reformer inlet (b & d)

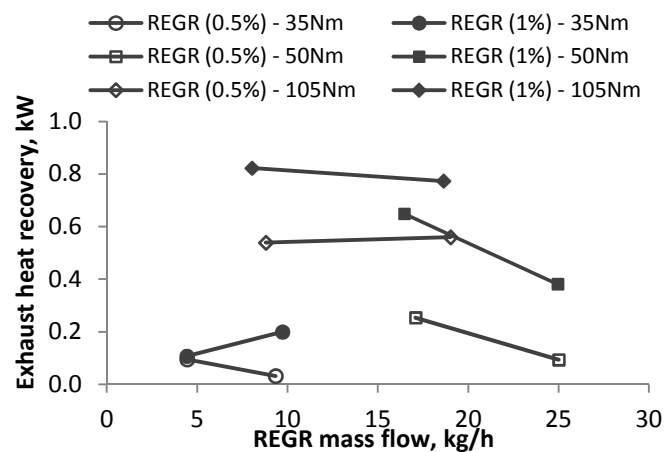
293 3.3 Exhaust energy recovery

294 *First law analysis - Exhaust stream energy:* Under normal engine operating conditions, i.e. when there is
 295 no reforming, the exhaust stream temperature drops (by some amount ΔT) as it passes across the
 296 reformer due to heat loss to the atmosphere. This is perhaps an obvious statement; however it is
 297 necessary to consider this heat loss when estimating the amount of exhaust energy recovery achieved
 298 by the reformer. When operating with EGR or REGR at a given engine load and recirculation rate, the
 299 exhaust stream mass flow, composition, and temperature at the reformer inlet are very similar;
 300 therefore it may be assumed that the heat loss to atmosphere is the same under each condition.

301 When the reformer is switched on there will be a greater exhaust stream temperature differential
 302 (ΔT_{REGR}) if energy is extracted by the overall endothermic reforming process. This means that the
 303 exhaust stream temperature drop due to reforming, ΔT_{Ref} can be estimated for each condition using
 304 $\Delta T_{Ref} = \Delta T_{REGR} - \Delta T_{EGR}$. The rate of exhaust heat recovery is then approximately equal to the change in
 305 enthalpy of the exhaust gases as they drop in temperature by ΔT_{Ref} , and is calculated using equation (7).
 306 The specific heat capacity of the exhaust stream, c_{exh} , was calculated for the mixture of nitrogen, CO₂
 307 and steam (post-TWC composition) at the average of the pre- and post-reformer exhaust stream
 308 temperature.

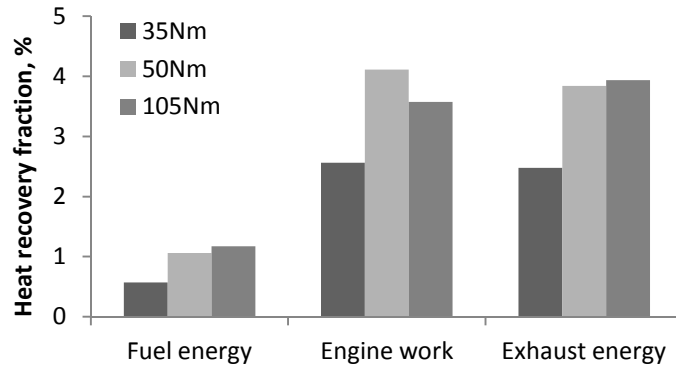
$$\text{Exhaust heat recovery, } \dot{Q} = \dot{H} = \dot{m}_{exh} \cdot \bar{c}_{p,exh} \cdot \Delta T_{Ref} \quad (\text{kW}) \quad (7)$$

309 The rate of exhaust stream heat recovery achieved by fuel reforming at each engine condition is plotted
 310 in Figure 8. The highest rate of heat recovery was achieved at the 105Nm engine condition when the
 311 reformer temperature was highest. This engine condition uses intermediate REGR mass flow rates and
 312 so the reformer's ability to recover exhaust energy is not compromised by high GHSV. At the 50Nm
 313 engine condition, increasing the REGR flow to the highest rate reduces heat recovery due to the
 314 combined effects of increased GHSV and lower exhaust stream temperature (increased charge dilution
 315 causes lower combustion and exhaust temperatures). In general, increasing the reformer fuel flow
 316 increases the amount of exhaust heat recovery.



317
 318 Figure 8 - Rate of exhaust stream heat recovery with fuel reforming

319 While considering the heat recovery in absolute terms is interesting, it is also important to put these
 320 values into perspective; Figure 9 presents the heat recovery as a fraction of the total fuel energy,
 321 engine effective work and pre-reformer exhaust stream energy. When working close to optimally at the
 322 50Nm and 105Nm conditions, the reformer is able to extract energy from the exhaust stream to
 323 recover around 1% of the total fuel energy supplied to the engine and reformer, which equates to
 324 between 3-4% of the effective engine work.



325
326 Figure 9 - Exhaust stream heat recovery as a fraction of total fuel energy, engine effective work and pre-
327 reformer exhaust energy

328 *Second law analysis - Exhaust stream exergy:* According to the second law of thermodynamics, exergy
329 represents the maximum amount of energy that can be extracted by bringing a system at temperature
330 T to the ambient temperature T_0 . The exergy of a fluid stream can be evaluated using equation (8) ¹⁶.
331 This considers the exergy of the enthalpy, kinetic energy and potential energy of the fluid stream. This
332 analysis was applied to the exhaust stream, which contains multiple gas species, using equation (9) to
333 calculate the ‘energy availability’ of the pre- and post-reformer exhaust gas, where \dot{N}_{exh} is the molar
334 flow of the exhaust stream (kmol/s) and n_i is the molar fraction of gas species i . In this case, T_0 was
335 taken as 298K.

$$\psi = (h - h_0) - T_0(s - s_0) + \frac{v^2}{2} + gz \quad (8)$$

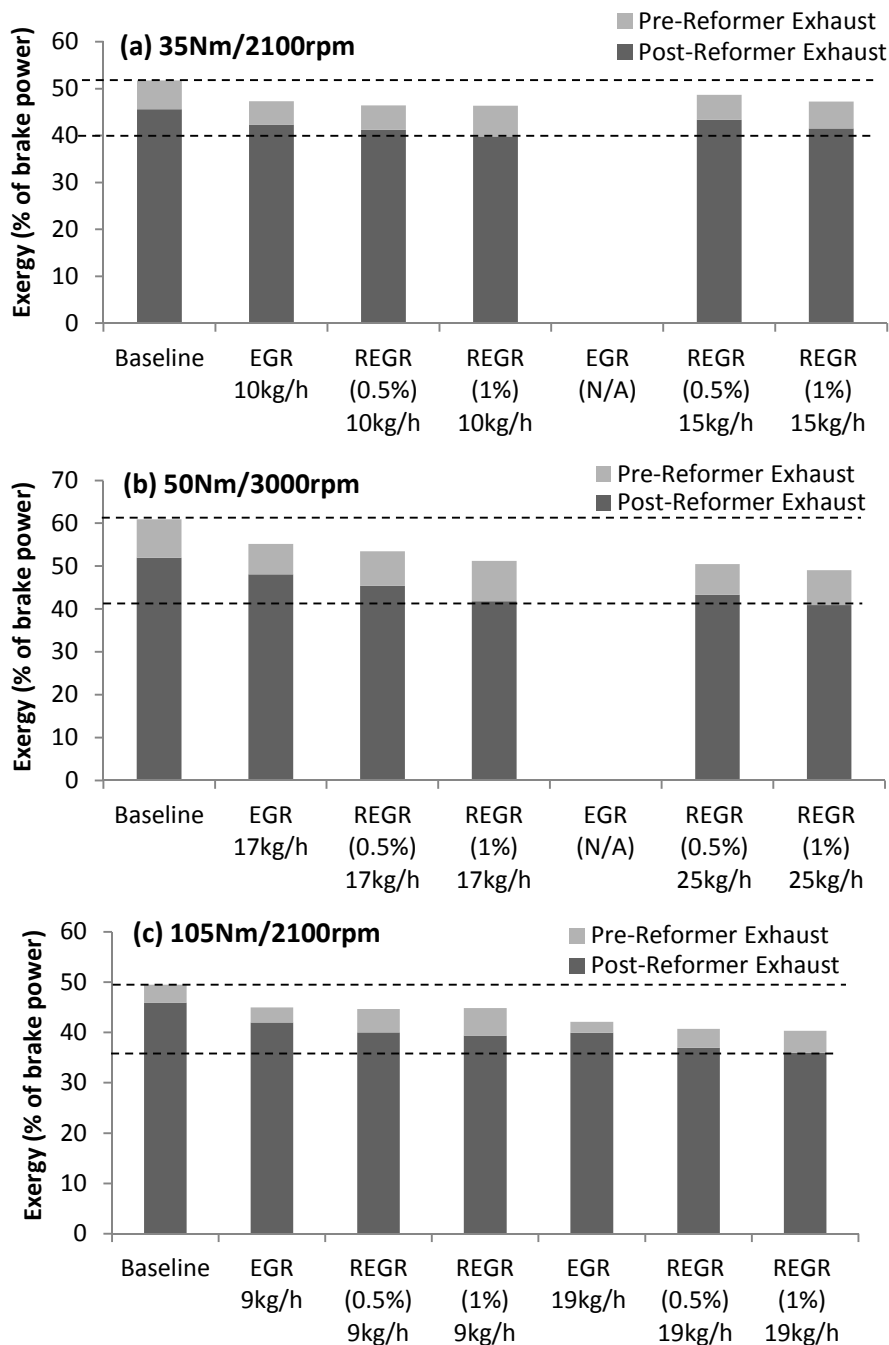
$$\psi_{exh} = \sum \dot{N}_{exh} \cdot n_i \cdot [(h_i - h_{i,0}) - T_0(s_i - s_{i,0})] \quad (\text{kW}) \quad (9)$$

336 There were various assumptions made during the calculation of exhaust exergy. These included: the
337 exhaust stream is a mixture of ideal gases; specific heat values are taken at the average process
338 temperature, and were calculated using 3rd order polynomial relationships from ¹⁶; the TWC catalyst
339 converts the exhaust stream to a mixture of inert gases (nitrogen, carbon dioxide and steam) with 100%
340 efficiency and therefore the exhaust contains no species with chemical potential energy; the exergy of
341 the kinetic and gravitational potential energy components of the exhaust stream are negligible.

342 As the reformer is designed to recover energy from the exhaust stream, there should be a reduction in
343 exergy, or available energy, across the reformer. A more efficient overall engine-reformer system
344 should also result in a reduction of the exhaust stream exergy (for a given load) at the reformer inlet.
345 This accounts for the influence of REGR on the engine and combustion efficiency, which directly
346 influences the exhaust exergy.

347 Figure 10 plots the pre- and post-reformer exhaust stream exergy, as a percentage of the
348 engine brake power, for each test condition at each engine load. These plots show the general trend for
349 reducing exhaust stream exergy with increasing dilution rate and reformed fuel fraction. In each case
350 the baseline condition exhaust exergy is highest; both EGR and REGR reduce the exhaust exergy. The

351 50Nm engine condition represents the highest 'relative' exergy with 60% of the brake power available
 352 for recovery; the highest absolute exergy was at the 105Nm condition.



353

354

355

356 Figure 10 - Comparing pre- and post-reformer exhaust stream exergy for a variety of engine conditions
 357 (a) 35Nm, (b) 50Nm and (c) 105Nm

358 **4. Conclusions**

359 A full-scale prototype exhaust gas fuel reformer has been coupled with a multi-cylinder GDI engine, and
 360 demonstrates that gasoline reforming is feasible as a thermochemical energy recovery technique at
 361 typical GDI engine exhaust temperature.

362 At higher exhaust temperatures, the reformer is capable of converting gasoline to hydrogen-rich gas in
363 an overall endothermic process while recovering some exhaust energy. Performance is borderline
364 effective at lower exhaust temperature (for engine conditions representing low vehicle speed); this
365 means that some reforming is possible which produces hydrogen that is beneficial to engine operation,
366 but a small amount of fuel energy is lost in the reforming process.

367 Speciation of reformat produced by the reformer at a range of engine conditions indicates a large
368 variation in reformat quality, with a strong dependence on process temperature and reactant
369 composition.

370 The outlook for fuel reforming may be improved should the trend for engine downsizing continue. By
371 placing a higher demand on the engine by downsizing, there is a shift to higher engine IMEPs for a given
372 road load and the mean exhaust temperature will be increased as a result. It can be concluded from this
373 study is that sustained (medium) engine loads, as used for motorway/highway driving, generate
374 conditions that favour fuel reforming; ultimately this means that exhaust energy recovery can be
375 achieved. The bias of many drive cycles to low engine speed/load conditions, and a high proportion of
376 warm-up time, mean that the fuel reformer is not likely show its full potential 'on cycle' but should
377 offer greater benefits for higher load and sustained driving conditions.

378 **Acknowledgments**

379 The work was funded by an industry-academia collaboration project, CO₂ Reduction through Emissions
380 Optimisation (CREO: ref. 400176/149), which is co-funded by the Innovate UK (Technology Strategy
381 Board). Daniel Fennell also received a postgraduate scholarship from this project. The reformer was
382 designed by Johnson Matthey PLC and developed in collaboration with the University of Birmingham
383 and Cambustion Ltd. Ford Motor Company is acknowledged for supplying the base engine and
384 associated parts. Internally, Carl Hingley and his team of technicians are acknowledged for their
385 assistance during the test cell construction.

386

387 **References**

- 388 1. D. Fennell, J. M. Herreros and A. Tsolakis, *Int J Hydrogen Energ*, 2014, **39**, 5153–5162.
- 389 2. P. Leung, A. Tsolakis, J. Rodriguez-Fernandez and S. Golunski, *Energy Environ. Sci.*, 2010, **3**, 780-
390 788.
- 391 3. Y. Jamal, T. Wagner and M. L. Wyszynski, *Int J Hydrogen Energ*, 1996, **21**, pp.507 - 519.
- 392 4. S. Peucheret, M. Feaviour and S. Golunski, *Appl Catal B-Environ*, 2006, **65**, 201-206.
- 393 5. A. A. Quader, J. E. Kirwan and M. J. Grieve, *SAE Paper*, 2003, 2003-01-1356.
- 394 6. K. D. Isherwood, J. R. Linna and P. J. Loftus, *SAE Paper*, 1998, 980939.
- 395 7. J. E. Kirwan, A. A. Quader and M. J. Grieve, *SAE Paper*, 2002, 2002-01-1011.
- 396 8. J. B. Green Jr., N. Domingo, J. M. E. Storey, R. M. Wagner, J. S. Armfield, L. Bromberg, D. R.
397 Cohn, A. Rabinovich and N. Alexeev, *SAE Paper*, 2000, 2000-01-2206.
- 398 9. E. J. Tully and J. B. Heywood, *SAE Paper*, 2003, 2003-01-0630.

- 399 10. E. D. Sall, D. A. Morgenstern, J. P. Fornango, J. W. Taylor, N. Chomic and J. Wheeler, *Energ Fuel*,
400 2013, **27**, 5579-5588.
- 401 11. C. Ji, X. Dai, B. Ju, S. Wang, B. Zhang, C. Liang and X. Liu, *Int J Hydrogen Energ*, 2012, **37**, 7860-
402 7868.
- 403 12. C. H. Bartholomew, *Appl Catal A-Gen*, 2001, **212**, 17-60.
- 404 13. S. Golunski, *Energ Environ Sci*, 2010, **3**, 1918-1923.
- 405 14. S. R. Gomes, N. Bion, G. Blanchard, S. Rousseau, V. Bellière-Baca, V. Harlé, D. Duprez and F.
406 Epron, *Appl Catal B-Environ*, 2011, **102**, 44-53.
- 407 15. S. R. Gomes, N. Bion, G. Blanchard, S. Rousseau, D. Duprez and F. Epron, *RSC Adv*, 2011, **1**, 109-
408 116.
- 409 16. Y. A. Cengel and M. A. Boles, *Thermodynamics: An Engineering Approach*, McGraw-Hill, 1998.

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