

Thermochemical recovery technology for improved modern engine fuel economy – part 1: analysis of a prototype exhaust gas fuel reformer

Fennell, D. , Herreros, J. M. , Tsolakis, A. , Cockle, K. , Pignon, J. and Millington, P.

Author post-print (accepted) deposited in CURVE April 2016

Original citation & hyperlink:

Fennell, D. , Herreros, J. M. , Tsolakis, A. , Cockle, K. , Pignon, J. and Millington, P. (2015) Thermochemical recovery technology for improved modern engine fuel economy – part 1: analysis of a prototype exhaust gas fuel reformer. RSC Advances, volume 5 : 35252-35261
<http://dx.doi.org/10.1039/C5RA03111G>

Copyright © and Moral Rights are retained by the author(s) and/ or other copyright owners. A copy can be downloaded for personal non-commercial research or study, without prior permission or charge. This item cannot be reproduced or quoted extensively from without first obtaining permission in writing from the copyright holder(s). The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the copyright holders.

This document is the author's post-print version, incorporating any revisions agreed during the peer-review process. Some differences between the published version and this version may remain and you are advised to consult the published version if you wish to cite from it.

CURVE is the Institutional Repository for Coventry University

<http://curve.coventry.ac.uk/open>

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

3 D. Fennell ^a, J. Herreros ^a, A. Tsolakis ^a, K. Cockle ^b, J. Pignon ^b, P. Millington ^b

4 ^aSchool of Mechanical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT

5 ^bJohnson Matthey Technology Centre, Blount's Court, Sonning Common, Reading, RG4 9NH

6 * Corresponding author: a.tsolakis@bham.ac.uk

7 Tel: +44 121 414 4170

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 emissions ¹⁻³. 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 studies ⁴ 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 from ⁵
 66

67 Other classifications of reformer have been researched for on-board hydrogen generation in the past.
 68 Partial oxidation reformers ⁵⁻⁷ 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-fuelled ¹⁰ and gasoline-fuelled ¹¹ 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 °C ¹⁰. This makes ethanol reforming feasible over most of the
80 operating range of a SI engine.

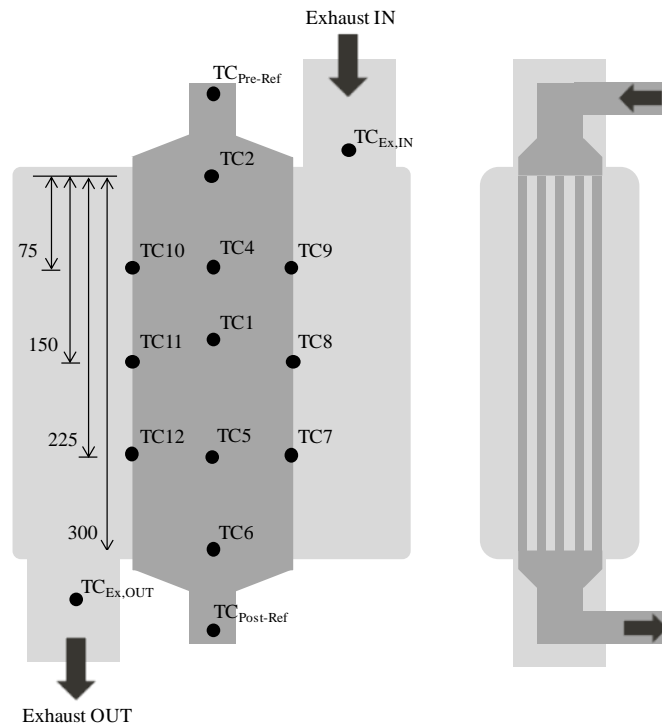
81 The gasoline reformer has potential for more widespread use than ethanol and E85 but greater
82 technical barriers to overcome, most notably with respect to achieving effective performance at
83 sufficiently low temperature to be feasible with the gasoline engine exhaust stream. Because reformer
84 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 Golunski ¹³ 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 study ¹ 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 was designed by Johnson Matthey and it consists of a stack of five metallic catalyst plates
106 coated with 3.6g/in³ of ceramic support (Ceria-Zirconia-Alumina) loaded with 3.3% Platinum - 1.7%
107 Rhodium. Each catalyst is mounted between two finned stainless steel plates used to seal it from the
108 exhaust stream. The reformer plate assembly was designed to ensure high heat transfer from the hot
109 exhaust gas to the catalyst, using fins on the stainless steel surround for increased surface area and a
110 narrow catalyst construction only four cells thick. The exhaust stream flows perpendicularly over the
111 reformer plate stack, which is positioned after the TWC. The reformer feed gas is extracted from the
112 exhaust stream before the TWC, mixed with gasoline, and routed around the outer skin of the TWC to
113 assist with fuel vaporisation and feed gas pre-heating. The required flow rate of gasoline was injected
114 into the reformer feed gas by varying the pulse-width of a solenoid fuel injector, typically used in port
115 injection engines, operating at a fixed frequency of 30Hz. The injector was mounted to the reformer
116 with a manifold cooled by engine water to protect the injector from high exhaust system temperatures.
117 11 thermocouples were distributed over the middle reformer plate according to schematic Figure 1,
118 with additional thermocouples in the feed gas, product gas, and exhaust stream before and after
119 passing over the reformer assembly.



120
121 Figure 1 - Reformer schematic indicating thermocouples (TC) locations on the central reformer plate
122 and in the exhaust stream

123 *Reformer installation:* The reformer was installed with a turbocharged 2L GDI engine, positioned in the
124 exhaust stream after the TWC. The REGR system installation used a 'high pressure' recirculation
125 configuration, inducting reformat directly into the intake manifold. The system consisted of an

126 integrated DC motor controlled EGR valve and cooler, and an additional cooler, all supplied with engine
127 coolant to maintain acceptable gas and component temperatures.

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

137 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

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

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

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

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

161 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

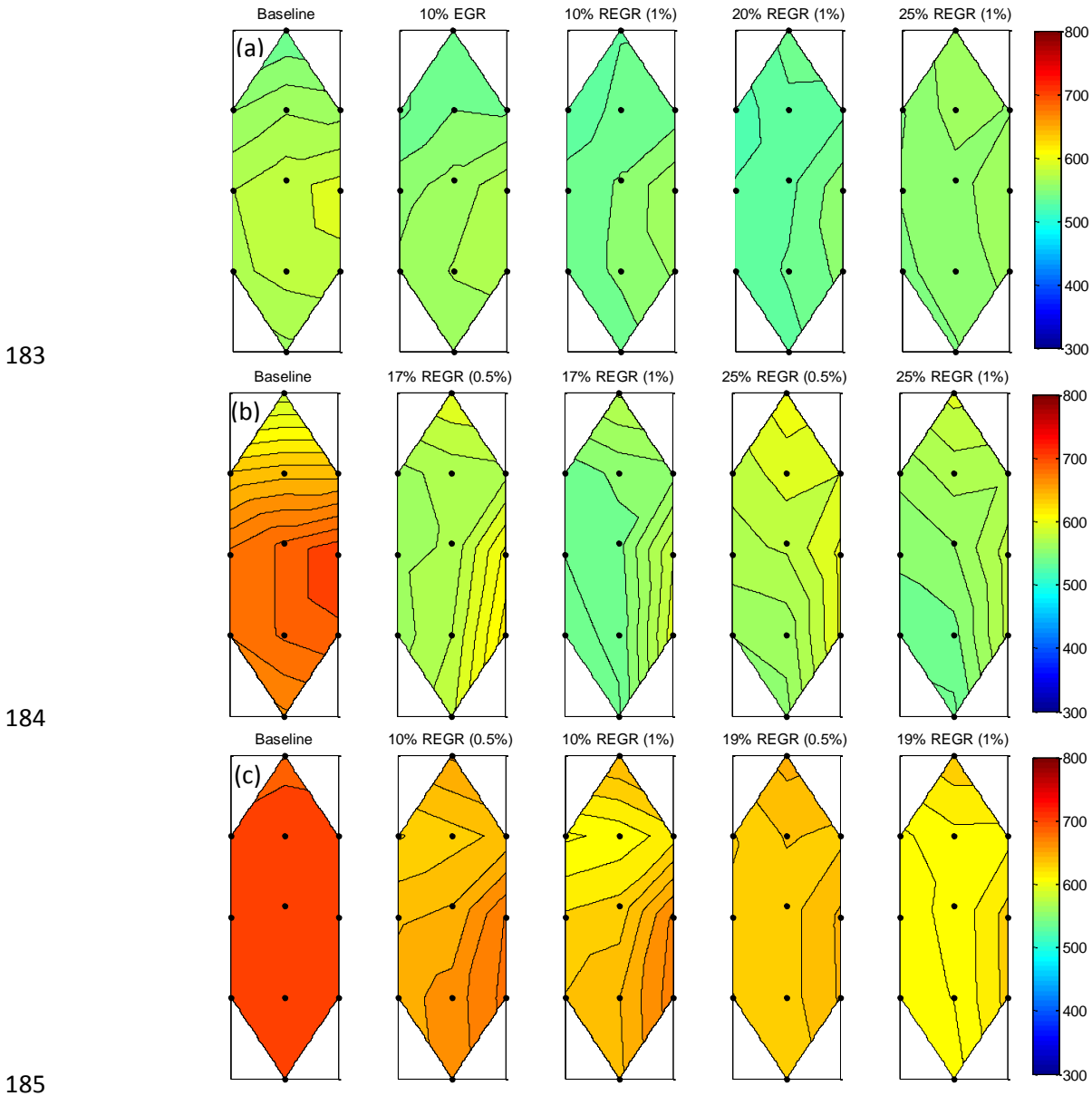
162 3. Results and discussion

163 3.1. Reformate characteristics

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

170 At the lowest temperature condition (35Nm/2100rpm) the plate temperatures drop as the REGR flow is
 171 increased up to 20% due to reforming activity. There is also a slight cooling effect just by flowing gas
 172 through the reformer (i.e. with EGR), analogous to a forced-convection cooling process. At the highest
 173 REGR flow rate there is a slight increase in reformer temperature with a more even distribution. This is
 174 the result of multiple effects associated with increasing the flow rate: more oxygen is available for fuel
 175 oxidation which increases the gas temperature in the front of the reformer; the high flow rate moves
 176 the high temperature gas along the reformer more quickly resulting in the more even distribution; and
 177 reforming activity tends to be lower as the flow rate increases.

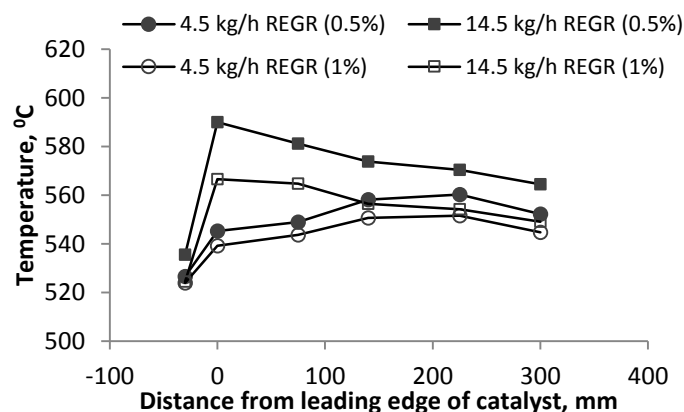
178 At the two higher engine load conditions the reformer is heated to significantly higher temperature
 179 when there is no REGR flow (baseline condition). Increasing either the REGR flow or the fuel
 180 concentration lowers the reformer temperature. Both of these changes increase the availability of fuel
 181 while, importantly, at sufficiently high temperature for the endothermic reforming reactions to be
 182 feasible. Again, increasing the REGR flow rate results in a more even temperature distribution.



186 Figure 2 – Temperature ($^{\circ}\text{C}$) distribution across the middle reformer plate at a) 35Nm, b) 50Nm and c)
 187 105Nm engine conditions, for a range of REGR concentrations (vol.) in the intake charge with either
 188 0.5% or 1% (vol.) gasoline in the reformer feed gas

189
 190 *Linear reformer temperature profiles:* Figure 3 compares the linear reformer temperature profiles while
 191 reforming with two different mass flows, 4.5 and 14.5kg/h - this equates to 10% and 25% REGR in terms
 192 of the dilution rate at the 35Nm/2100rpm engine condition. Temperature profiles are included for 0.5%

193 and 1% fuel in the reformer feed gas. At low reactant mass flow rate in the reformer, there was very
 194 little heating due to exothermic reactions in the front of the catalyst. There was no indication of
 195 endothermic reforming cooling the reformer. It appears that a small amount of reforming occurred in
 196 the first 75mm of the reformer as the temperature remains approximately constant. After this the
 197 temperature increased due to heating by the main engine exhaust stream. At the higher reactant flow
 198 rate there was a greater quantity of fuel and oxygen passing through the reformer which led to a larger
 199 temperature increase at the front face. The combination of higher temperature and more fuel being
 200 available for reforming meant that there was a clear drop in temperature along the length of the
 201 reformer due to endothermic reforming reactions.



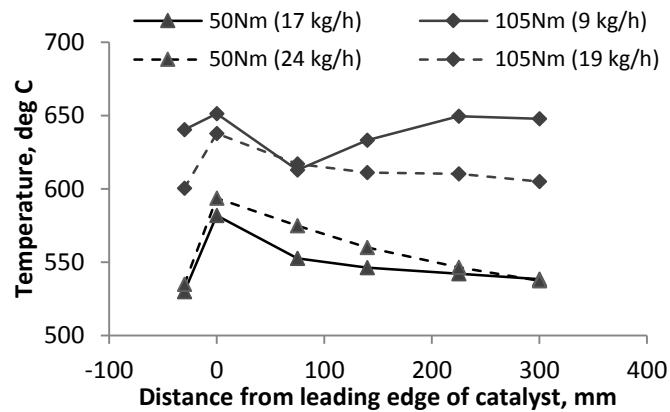
202 Figure 3 – Linear reformer temperature profile at the low temperature (35Nm/2100rpm) condition.
 203

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

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

217 When the reformer flow is low and the reformer plate temperature is relatively high at the inlet, 650°C
 218 at the 105Nm condition, most of the reforming occurs in the first section of the reformer and is

219 followed by re-heating. This implies that the reformer is able to process more fuel than is being
220 supplied at the low flow condition.



221
222 Figure 4 - Linear reformer plate temperature profiles for high and low REGR flows at two engine
223 conditions (1% feed gas fuel concentration in each case)

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

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

235 *Reformate speciation:* Maximum hydrogen production was observed when the consumption of steam
236 was greatest, which indicates successful promotion of the steam reforming reaction (Fig. 5). This
237 occurred at the 50Nm/3000rpm engine condition, when there was 11% hydrogen produced and 6% un-
238 reacted steam measured in the reformate, and there was a combination of high temperature and
239 intermediate reactant flow rate.

240 Some CO₂ can be expected to be produced by oxidation and WGS reactions, and may be consumed by
241 the dry reforming reaction. The CO₂ concentration in the reformate was relatively consistent at most
242 test points but was reduced slightly for low REGR mass flow rates. It should be noted that for a given
243 engine load, at lower REGR mass flows the reformer plate temperatures are higher. This means the
244 reversible WGS reaction has a smaller equilibrium constant, is therefore less favourable towards the
245 reaction products, and so less hydrogen and CO₂ are produced by this reaction.

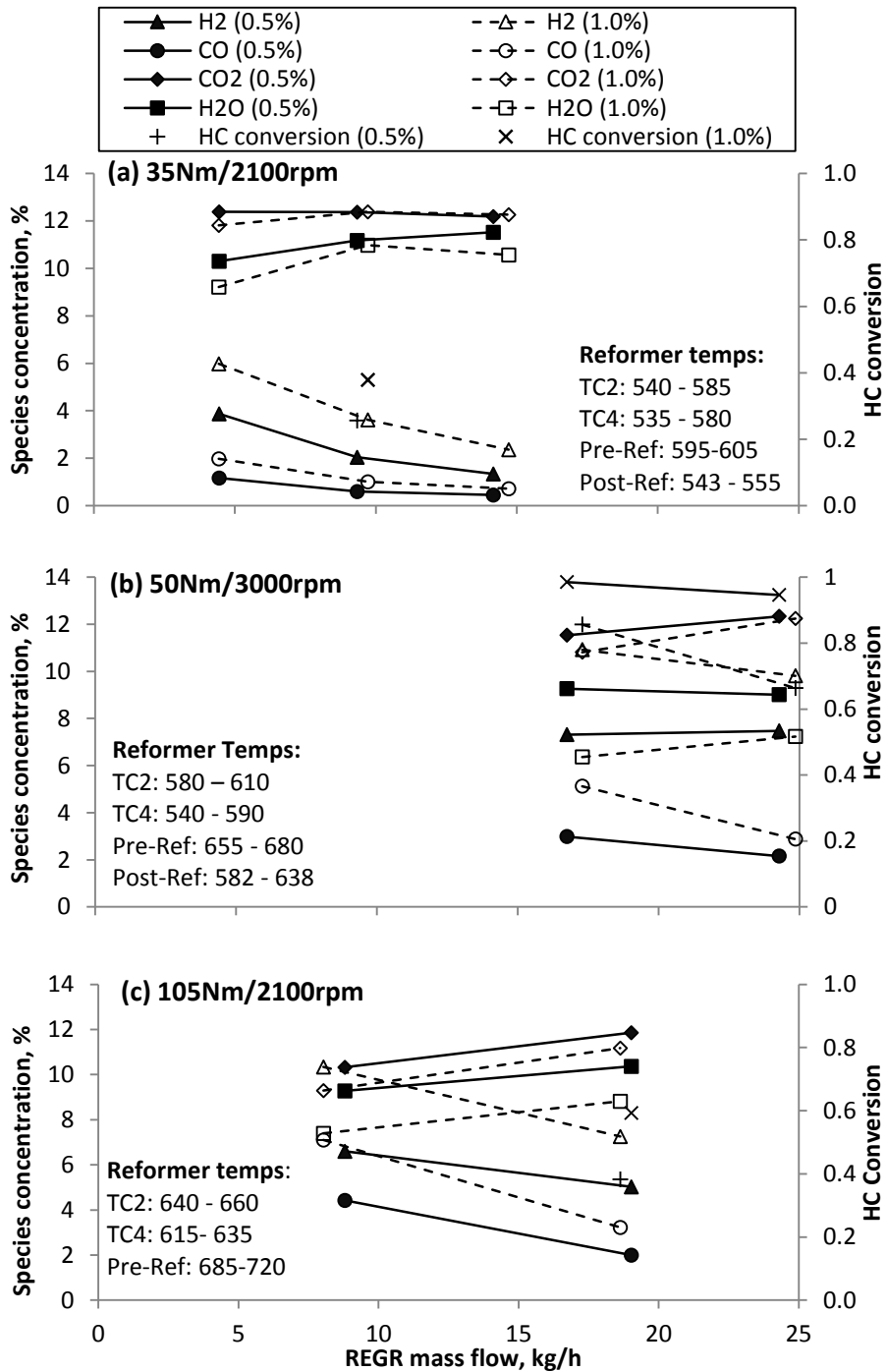


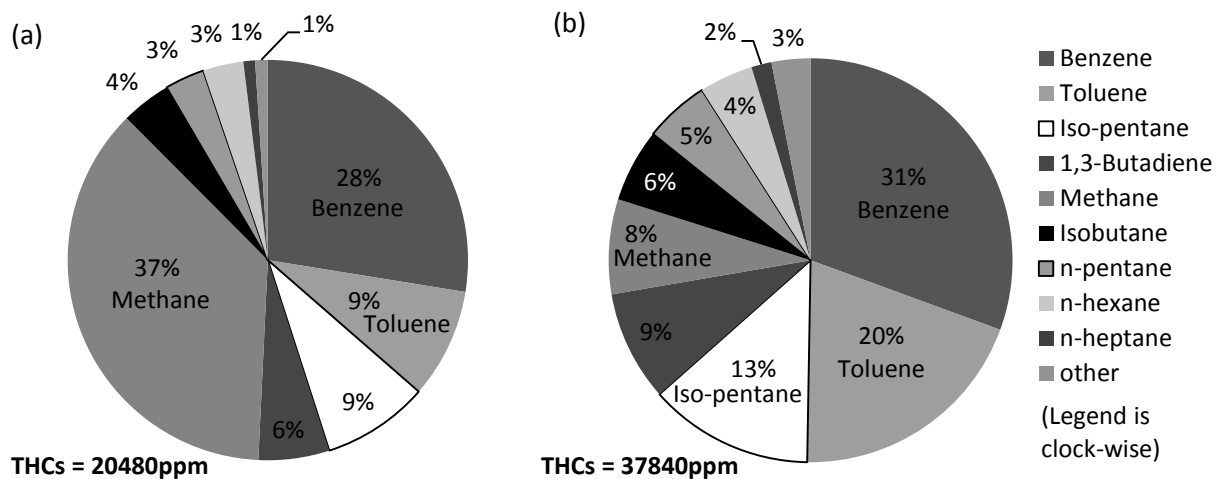
Figure 5 - Reformate species concentrations at various engine conditions (a) 35Nm, (b) 50Nm and (c) 105Nm

246
 247 *Hydrocarbon speciation:* The proportion of HCs that breakthrough the reformer increases with REGR
 248 flow rate; therefore at 17kg/h REGR (Figure 6a) there is a lower total HC (THC) concentration. The
 249 calibration gas used contains many of the major components (Table 2) of gasoline and there were no
 250 significant peaks in the chromatogram spectrum unaccounted for.

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

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

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



265 Figure 6 - Proportion of HC species of the total HCs in reformat as measured by GC-FID at
 266 50Nm/3000rpm with REGR (1% fuel): 17 kg/h (a) and 24 kg/h (b)

267 3.2 Reformer process efficiency

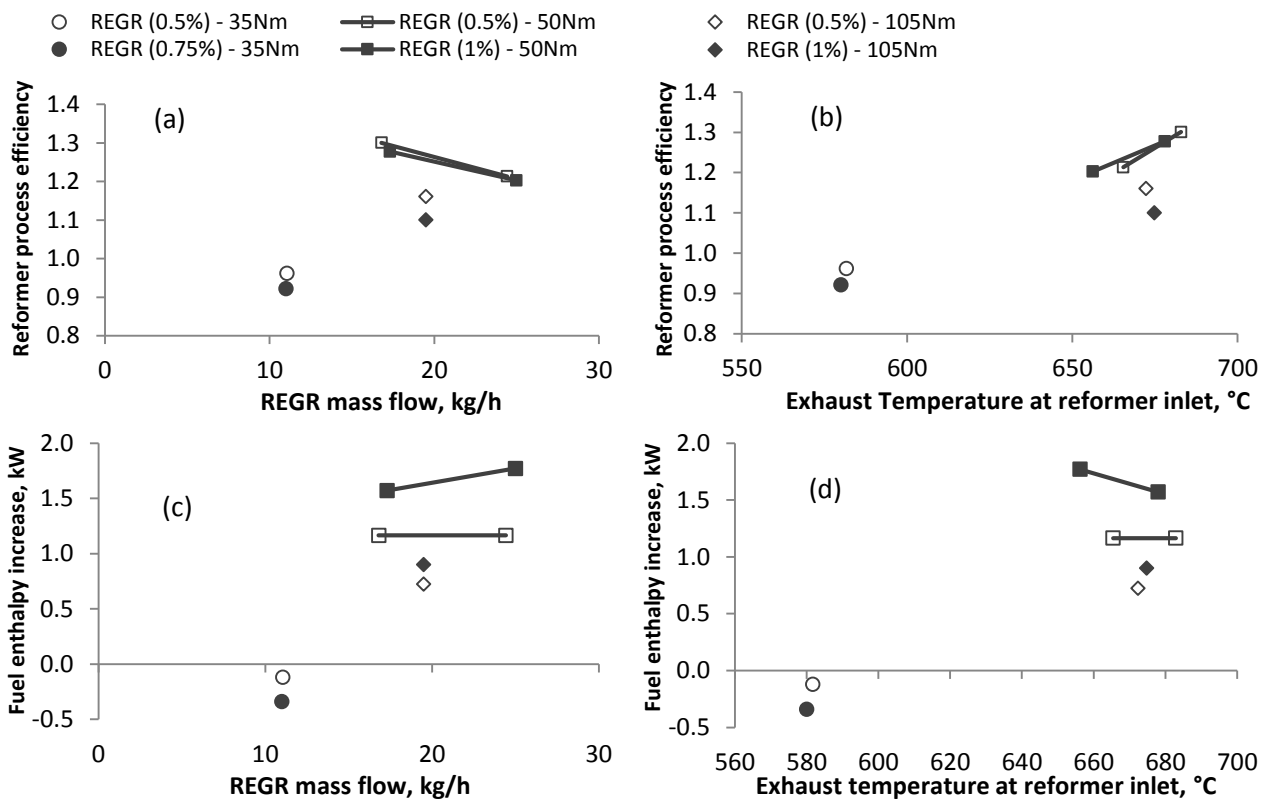
268 The effectiveness of the reformer can be analysed by calculating the reformer process efficiency using
 269 Equation (7). In this equation the HCs and CO contained in the engine exhaust gas which is fed in the
 270 reformer are not included in the calculation of the reformer efficiency. However,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

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

277

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

285



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

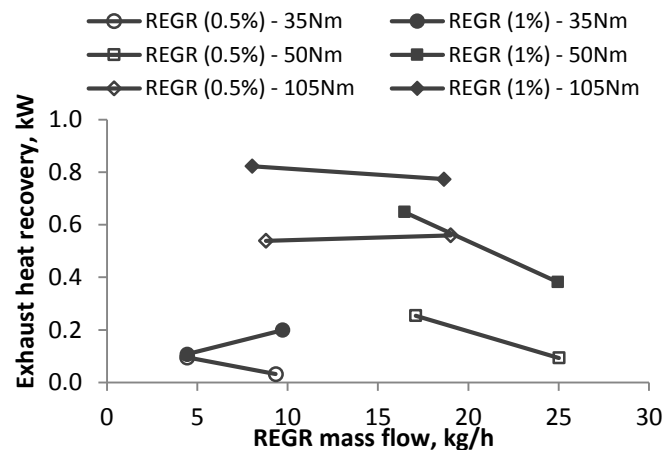
288 3.3 Exhaust energy recovery

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

296 When the reformer is switched on there will be a greater exhaust stream temperature differential
 297 (ΔT_{REGR}) if energy is extracted by the overall endothermic reforming process. This means that the
 298 exhaust stream temperature drop due to reforming, ΔT_{Ref} can be estimated for each condition using
 299 $\Delta T_{Ref} = \Delta T_{REGR} - \Delta T_{EGR}$. The rate of exhaust heat recovery is then approximately equal to the change in
 300 enthalpy of the exhaust gases as they drop in temperature by ΔT_{Ref} , and is calculated using equation (7).
 301 The specific heat capacity of the exhaust stream, c_{exh} , was calculated for the mixture of nitrogen, CO₂
 302 and steam (post-TWC composition) at the average of the pre- and post-reformer exhaust stream
 303 temperature.

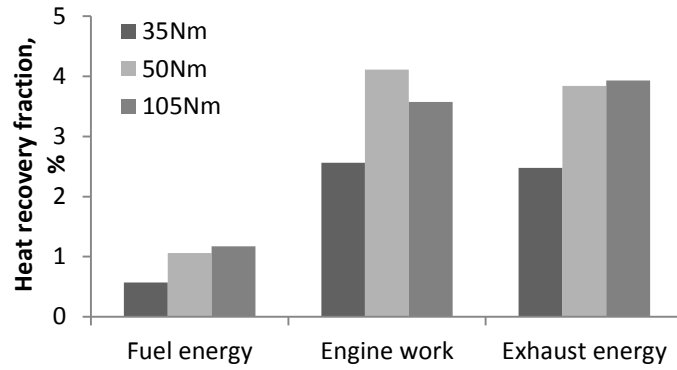
$$\text{Exhaust heat recovery, } \dot{Q} = \dot{H} = \dot{m}_{exh} \cdot \bar{c}_{p,exh} \cdot \Delta T_{Ref} \quad (\text{kW}) \quad (7)$$

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



312
 313 Figure 8 - Rate of exhaust stream heat recovery with fuel reforming

314 While considering the heat recovery in absolute terms is interesting, it is also important to put these
 315 values into perspective; Figure 9 presents the heat recovery as a fraction of the total fuel energy,
 316 engine effective work and pre-reformer exhaust stream energy. When working close to optimally at the
 317 50Nm and 105Nm conditions, the reformer is able to extract energy from the exhaust stream to
 318 recover around 1% of the total fuel energy supplied to the engine and reformer, which equates to
 319 between 3-4% of the effective engine work.



320
 321 Figure 9 - Exhaust stream heat recovery as a fraction of total fuel energy, engine effective work and pre-
 322 reformer exhaust energy

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

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

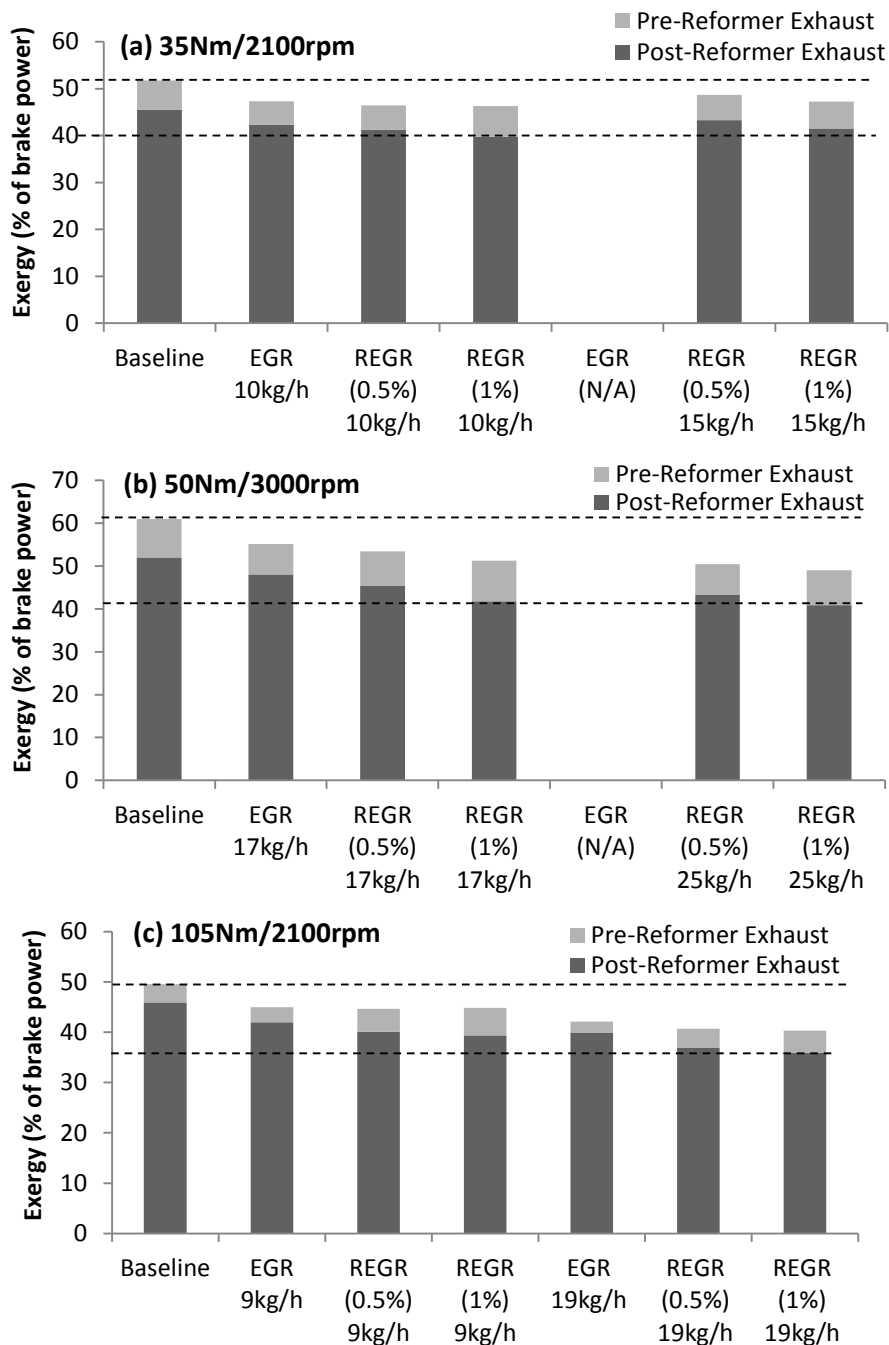
$$\psi_{exh} = \sum \dot{N}_{exh} \cdot n_i \cdot [(h_i - h_{i,0}) - T_0(s_i - s_{i,0})] \quad (\text{kW}) \quad (9)$$

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

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

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

346 50Nm engine condition represents the highest 'relative' exergy with 60% of the brake power available
 347 for recovery; the highest absolute exergy was at the 105Nm condition.



348

349

350

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

353 **4. Conclusions**

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

357 At higher exhaust temperatures, the reformer is capable of converting gasoline to hydrogen-rich gas in
358 an overall endothermic process while recovering some exhaust energy. Performance is borderline
359 effective at lower exhaust temperature (for engine conditions representing low vehicle speed); this
360 means that some reforming is possible which produces hydrogen that is beneficial to engine operation,
361 but a small amount of fuel energy is lost in the reforming process. The technology has further heat
362 recovery potential as there is still a significant exergy associated with the exhaust stream. Speciation of
363 reformate produced by the reformer at a range of engine conditions indicates a large variation in
364 reformate quality, with a strong dependence on process temperature and reactant composition.
365 The outlook for fuel reforming may be improved should the trend for engine downsizing continue. By
366 placing a higher demand on the engine by downsizing, there is a shift to higher engine IMEPs for a given
367 road load and the mean exhaust temperature will be increased as a result. It can be concluded from this
368 study is that sustained (medium) engine loads, as used for motorway/highway driving, generate
369 conditions that favour fuel reforming; ultimately this means that exhaust energy recovery can be
370 achieved. The bias of many drive cycles to low engine speed/load conditions, and a high proportion of
371 warm-up time, mean that the fuel reformer is not likely show its full potential 'on cycle' but should
372 offer greater benefits for higher load and sustained driving conditions.

373 **Acknowledgments**

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

381

382 **References**

- 383 1. D. Fennell, J. M. Herreros and A. Tsolakis, *Int J Hydrogen Energ*, 2014, **39**, 5153–5162.
- 384 2. P. Leung, A. Tsolakis, J. Rodriguez-Fernandez and S. Golunski, *Energy Environ. Sci.*, 2010, **3**, 780-
385 788.
- 386 3. Y. Jamal, T. Wagner and M. L. Wyszynski, *Int J Hydrogen Energ*, 1996, **21**, pp.507 - 519.
- 387 4. S. Peucheret, M. Feaviour and S. Golunski, *Appl Catal B-Environ*, 2006, **65**, 201-206.
- 388 5. A. A. Quader, J. E. Kirwan and M. J. Grieve, *SAE Paper*, 2003, 2003-01-1356.
- 389 6. K. D. Isherwood, J. R. Linna and P. J. Loftus, *SAE Paper*, 1998, 980939.
- 390 7. J. E. Kirwan, A. A. Quader and M. J. Grieve, *SAE Paper*, 2002, 2002-01-1011.
- 391 8. J. B. Green Jr., N. Domingo, J. M. E. Storey, R. M. Wagner, J. S. Armfield, L. Bromberg, D. R.
392 Cohn, A. Rabinovich and N. Alexeev, *SAE Paper*, 2000, 2000-01-2206.
- 393 9. E. J. Tully and J. B. Heywood, *SAE Paper*, 2003, 2003-01-0630.

- 394 10. E. D. Sall, D. A. Morgenstern, J. P. Fornango, J. W. Taylor, N. Chomic and J. Wheeler, *Energ Fuel*,
395 2013, **27**, 5579-5588.
- 396 11. C. Ji, X. Dai, B. Ju, S. Wang, B. Zhang, C. Liang and X. Liu, *Int J Hydrogen Energ*, 2012, **37**, 7860-
397 7868.
- 398 12. C. H. Bartholomew, *Appl Catal A-Gen*, 2001, **212**, 17-60.
- 399 13. S. Golunski, *Energ Environ Sci*, 2010, **3**, 1918-1923.
- 400 14. S. R. Gomes, N. Bion, G. Blanchard, S. Rousseau, V. Bellière-Baca, V. Harlé, D. Duprez and F.
401 Epron, *Appl Catal B-Environ*, 2011, **102**, 44-53.
- 402 15. S. R. Gomes, N. Bion, G. Blanchard, S. Rousseau, D. Duprez and F. Epron, *RSC Adv*, 2011, **1**, 109-
403 116.
- 404 16. Y. A. Cengel and M. A. Boles, *Thermodynamics: An Engineering Approach*, McGraw-Hill, 1998.

405

406