

## Fuel reforming in internal combustion engines



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### ABSTRACT

This article offers a comprehensive overview of research on fuel reforming in internal combustion engines (ICE). It includes a historical perspective of research in this field, a discussion on the considerations to be made prior to choosing a primary fuel for reforming purposes, and the main processes in fuel reforming. Steam reforming offers a moderate degree of thermochemical recuperation and is applicable to methanol and ethanol feeding. Reforming with air reduces the degree of recuperation, but opens up the use of heavier fuels such as gasoline and diesel fuel. Dry reforming (with CO<sub>2</sub>) offers the best recuperation but is prone to fast coking. The choice of catalyst and the expected side reactions for each fuel are also discussed. While there is extensive literature on steam reforming catalysts and kinetics at atmospheric pressure, studies at higher pressures and/or on decomposition reactions are very few. The thermodynamics of fuel reforming in ICE and simulation approaches are also discussed. The paper also reports on engineering aspects of fuel reformer design and provides an overview of engines with thermo-chemical recuperation (TCR), fuel supply, and load control strategies in ICE with TCR. In-cylinder fuel reforming as well as application of fuel reforming for performance improvement of emission aftertreatment systems are subsequently discussed. This overview reveals ongoing diverse research activities in the field of onboard fuel reforming. However, several problems, including reformate burning velocity at typical for ICE conditions, in-cylinder behavior of directly injected reformates and particle formation still need to be addressed. A discussion on some of these unresolved issues is attempted herein.

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## 1. Introduction

### 1.1. Required improvement of energy efficiency and emission mitigation

Transportation is responsible for the majority of global fuel consumption. According to the data from the International Energy Agency (IEA) [1], about 26% of all energy-related CO<sub>2</sub> emissions in 2007 were caused by transportation. This value is likely to increase in future unless special measures are adopted. Following the recommendation of the United Nations Intergovernmental Panel on Climate Change (IPCC), by 2050, the annual global greenhouse gas (GHG) emissions must be reduced by 50 - 85% of the emission levels recorded in 2000. This will result in limiting the long-term global heating to 2.0 - 2.4 deg. C [2]. However, more recent studies have indicated that climate change is occurring faster than previously expected and that even a 50% reduction in global GHG emissions by 2050 may not be enough [3].

In 2006, road transportation was responsible for about three-quarters of the global energy consumption in the transportation segment [4]. In Europe this number is even higher and reached 82.5% in 2009 [5]. Nowadays, road transportation is almost entirely dependent (~ 95%) on crude oil [6]. Therefore, to meet GHG emission targets and decrease oil dependency, the overall energy consumption of road vehicles must be significantly reduced. The major challenge in reaching this goal is to reduce vehicle carbon emissions without disrupting transportation patterns and population mobility.

According to the World Business Council for Sustainable Development (WBCSD), the vehicle GHG intensity is determined from the following factors [7]:

- 1) The amount of energy required by an average vehicle to perform a given amount of transport activity in each transportation mode. This factor depends on the energy consumption of the vehicle.
- 2) The carbon content of the used fuel together with its production and distribution methods.
- 3) The total volume of transportation activity, which is dependent on the number of operating vehicles and their usage patterns. This is a function of consumer demand.
- 4) The modal composition of transportation activity, which is dependent on consumer choice, mode pricing, and fiscal measures that influence mode selection.

The first two modes have the biggest impact on vehicle GHG intensity. According to the IEA, 80% of the necessary reduction in GHG emissions can be achieved by improving vehicle energy efficiency and fuel decarbonization. This provides a strong incentive for research and development of new technologies based on alternative energy sources and energy carriers [8].

### 1.2. Thermochemical recuperation as a method of simultaneous waste heat recovery and hydrogen production

Intensive research aimed at the development of internal combustion engine (ICE)-based propulsion systems with 60% brake thermal efficiency and ultra-low pollutant emissions is ongoing [9–12]. There is wide consensus that waste heat recovery (WHR) is

necessary in achieving this ambitious goal [12,13]. Various known WHR methods, including turbocharging [14], turbo-compounding [15], thermo-electrics [16], the Rankine cycle [17], in-cylinder WHR [18], and cabin heating and cooling [19] are being developed at different rates of intensity. The most mature and widely applied WHR method is turbocharging [8]. Waste heat can also be used to sustain endothermic reactions of fuel reforming, a method often referred to as thermochemical recuperation (TCR) [20]. TCR presents two major advantages over turbocharging: firstly, the amount of utilized energy is not limited by isentropic expansion and secondly, the gaseous reforming product mixture (reformate) usually comprises a high hydrogen content to afford increased flame velocity, wider flammability limits, and reduced combustion irreversibility [21]. Hence, TCR improves the ICE efficiency because of the increased heating value of the fuel as a result of WHR as well as lean burning options, approaching the efficiency of an ideal Otto cycle and providing the possibility of applying higher compression ratios.

Notably, fuel reforming through TCR allows convenient vehicle fueling with a liquid fuel, while the engine is fed by a gaseous H<sub>2</sub>-rich reformate produced onboard. Thus, the major issues related to H<sub>2</sub> use as an alternative fuel, such as fueling infrastructure and H<sub>2</sub> storage onboard a vehicle, are eliminated. The challenge of onboard H<sub>2</sub>-storage is directly related to the physical properties of hydrogen: a very low volumetric energy content (10.3 MJ/m<sup>3</sup> at 1 bar or ~ 3000 MJ/m<sup>3</sup> at 350 bar compared to 33,750 MJ/m<sup>3</sup> for gasoline) and extremely low boiling point (20 K). Fig. 1 compares various hydrogen storage technologies with reference to conventional and some alternative liquid fuels. None of the H<sub>2</sub> storage methods reach the volumetric energy densities of gasoline and other liquid fuels to provide a vehicle driving range comparable to that afforded by conventional and liquid alternative fuels.

Wide flammability limits and very low ignition energy of H<sub>2</sub> present storage safety concerns at limited ventilation conditions because of the danger of explosive mixture formation that may cause severe damage. However, this is partially compensated for by a very high mass diffusivity of H<sub>2</sub> (0.78 m·10<sup>-4</sup>/s), which is an order of magnitude higher than that of gasoline (0.07 m·10<sup>-4</sup>/s). Storage of syngas (mainly hydrogen and carbon monoxide) has also proven to be problematic for the same reasons. The hazards of pure H<sub>2</sub> and syngas storage and transport hamper the commercialization and market penetration of hydrogen- and syngas-fed engines. Taking this into account, the production of H<sub>2</sub> or H<sub>2</sub>-rich gaseous fuel by onboard reforming of a liquid primary fuel with coincident WHR through TCR is attracting much attention. To date, works in this area have been reported by Dai et al. [22], He et al. [23], Ji et al. [24], Liao & Horng [25], Li et al. [26], Sall et al. [27], Tartakovsky et al. [28], Nguyen & Verhelst [29], among other.

Nowadays, TCR has been commercialized and is successfully used in various stationary applications, including gas turbines in power plants for distributed power generation [30–33] and furnaces [34]. Fuel reforming is being broadly studied as an onboard hydrogen production method for fuel cells. A comprehensive review of fuel reformers for fuel cells was performed by Pettersson & Westerholm [35]. Additionally, recent progress in this field was surveyed and analyzed in detail in review articles by Alves et al. [36], Xu et al. [37], Iulianelli et al. [38], Gur [39] and Timurkutluk et al. [40]. Proton-exchange membrane (PEM) fuel cells require pure hydrogen for their efficient operation as even small traces of CO result in degradation of

## Nomenclature

### Abbreviations

BTE	brake thermal efficiency
CAD	crank angle degree
CI	compression ignition
CNG	compressed natural gas
COV	coefficient of variation
DI	direct injection
DME	dimethyl ether
DPF	diesel particle filter
ED	ethanol decomposition
EGR	exhaust gas recirculation
FTP	federal test procedure
GHG	greenhouse gas
HC	hydrocarbons
HCCI	homogeneous charge compression ignition
HV	heating value
HWFET	highway fuel economy test
ICE	internal combustion engine
IEA	International Energy Agency
IMEP	indicatory mean effective pressure
IPCC	(United Nations) Intergovernmental Panel on Climate Change
IRFD	injector reference flow diameter
LHV	lower heating value
LPG	liquefied petroleum gas
MC	methanol conversion
MSR	methanol steam reforming
NVO	negative valve overlap
PEM	proton-exchange membrane
REGR	reformed exhaust gas recirculation
RON	research octane number
SCR	selective catalytic reduction
S/E	steam-to-ethanol ratio
SI	spark ignition
S/M	steam-to-methanol ratio
SOFC	solid oxide fuel cell
SR	steam reforming
SRE	steam reforming of ethanol
TCR	thermo-chemical recuperation
WBSCD	World Business Council for Sustainable Development
WGS	water-gas-shift reaction
WOT	wide-open throttle

### Symbols

$f$	fugacity
$H$	enthalpy
$G$	Gibbs free energy
$n$	engine rotation speed
$P$	power
$R$	molar gas constant
$S$	burning velocity
$T$	temperature
$x$	CO selectivity
$z$	CH <sub>4</sub> selectivity

### Greek symbols

$\lambda$	air excess factor
$\varphi$	equivalence ratio
$\eta$	efficiency
$\theta$	flame propagation angle

### Subscripts

b	brake
comb	combustion
in	primary reactants
r	reaction
T	turbulent
L	laminar

fuel cell performance. CO poisons the anode reaction through preferential adsorption onto the platinum surface, thereby blocking active sites [41]. To afford onboard pure H<sub>2</sub> production, several research groups have used membrane reformers to incorporate H<sub>2</sub> separation with selective Pd and Pd-alloy membranes. To supply the required energy, Sheintuch et al. used auto-thermal membrane reformers [42–44] in which the reformer effluents are mixed with air and oxidized in a catalytic reactor imbedded within the reformer. Compared to the strict requirement of high-purity hydrogen in fuel cells, ICE is much more flexible and can effectively burn different mixtures of hydrogen, carbon monoxide, and other gases. This characteristic greatly reduces the cost of energy produced from renewable fuels [45]. Thus, for ICE applications, the reforming conditions should be optimized to achieve a reformat composition that is favorable as an ICE fuel.

This overview focuses on recent advances in fuel reforming in internal combustion engines. The paper begins with a short historical retrospective (Section 2), followed by a discussion on the fundamentals of fuel reforming (Section 3) and reformer design peculiarities (Section 4). ICEs with thermochemical recuperation, including fuel reforming for exhaust aftertreatment purposes and in-cylinder reforming are discussed in Sections 5–7. Section 8 focuses on considerations for fuel reforming in ICE. Finally, some open questions and future research directions are summarized in Section 9.

## 2. Historical retrospective

Initial research in the field of onboard fuel reforming aimed at hydrogen generation began in the United States in the late 1960s and was mainly directed towards reducing pollutant emissions from spark-ignition engines [46]. Lee and Wimmer [46] were the first to demonstrate that a fuel gas (the name they gave to the reformat),

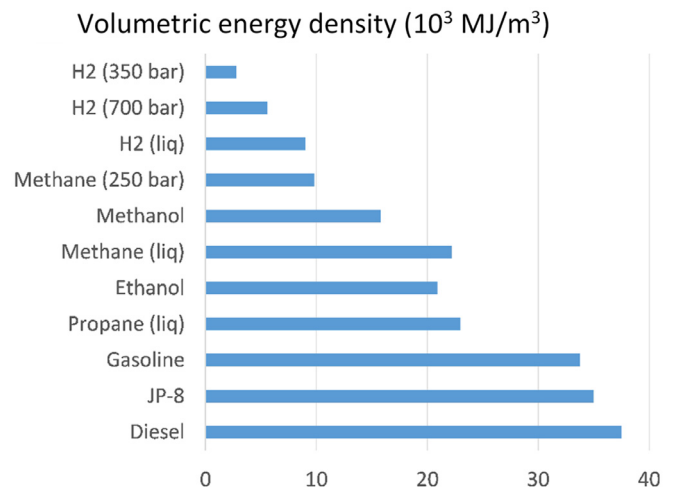


Fig. 1. Volumetric energy density of various fuels (10<sup>3</sup> MJ/m<sup>3</sup>).

which could be steam-reformed from a liquid fuel, exhibited better lean burning behavior and produced lower emissions than propane and methane. Various fuel reforming technologies were investigated in the 1970 s and 1980 s, including steam reforming (SR), decomposition (thermal dissociation), partial oxidation and exhaust gas fuel reforming [47].

Martin [48] was the first to consider a reformer and internal combustion engine as a total energy conversion system. He attempted to utilize waste heat from the engine to sustain the endothermic fuel reforming reactions and suggested catalytic SR of gasoline at a temperature of 893 K. Martin was also the first to theoretically predict the possibility of engine efficiency improvement from the increase in the reformate heating value and the possibility of pumping loss reduction. The latter is due to the wide flammability limits of a hydrogen-rich reformate. This makes the operation of an engine at partial loads with wide-open throttle (WOT) possible, thereby precluding the necessity for charge throttling. The benefits of fuel reforming are discussed below (Section 5).

Houseman and Cerini [49] applied a gasoline partial oxidation technique to produce hydrogen onboard an engine. They utilized partial oxidation over a nickel-based catalyst. The developed reformer exhibited a thermal efficiency of 78.5% (ratio of the net enthalpy of combustion of the reforming products to the net enthalpy of combustion of the primary fuel), corresponding to 96% of the maximum theoretical value. The process afforded H<sub>2</sub> and CO yields of 21.6 and 23.6% vol, respectively. Houseman and Cerini were the first to apply dual-fuel engine operation where the reformate gas was added to the engine intake manifold together with the gasoline-air mixture.

Research activities on exhaust gas fuel reforming also began in the 1970 s. Lindström [50] proposed that 5–50% of the engine exhaust gases could be conveyed to a reformer where they could mix with gasoline. He suggested that endothermic SR reactions, sustained by the enthalpy, CO<sub>2</sub> and steam content of the exhaust gases, would afford a gaseous fuel comprising H<sub>2</sub> and CO. Any additional energy required to sustain the endothermic reactions of gasoline reforming would be supplied by combustion of the gasoline or reformate fraction.

Another fuel that has received considerable attention is methanol. Methanol is a niche alternative fuel with no available fueling infrastructure to date. However, as a primary fuel for ICE with TCR, it has several important benefits. Methanol shows great potential as an alternative fuel as it can be produced from a variety of fossil and renewable feedstocks [51–53]. In addition, it is reformed at relatively low temperatures (523–573 K) [54,55], making efficient exhaust heat recovery possible. Pettersson & Sjöström [56] overviewed most of the research on methanol reforming for ICEs conducted up to the early 1990 s. Finegold [57] and Sakai et al. [58] even built cars with on-board methanol decomposition and reported up to 40% increase in energy efficiency compared to a gasoline-operated vehicle of similar type. Brinkman and Stebar [59] pointed out that the increased efficiency was a result of the beneficial properties of the H<sub>2</sub>-rich methanol reforming products, such as higher burning velocity and wider flammability limits, compared to gasoline. The main problems reported in these early studies were backfire and pre-ignition, coke formation on the reformer catalyst, cold start difficulties, engine power loss due to reduced air charging, and formaldehyde formation (in the cases of liquid methanol combustion). A few years later, in 1994, Jamal & Wyszynski [60] reviewed the use of H<sub>2</sub> and H<sub>2</sub>-enriched gasoline as fuels for SI engines. They also analyzed the techniques used to generate H<sub>2</sub> from liquid fuels such as gasoline and methanol on-board a vehicle and claimed that onboard H<sub>2</sub> generation from liquid fuels (hydrocarbons or alcohols) was technically feasible.

### 3. Fundamentals

#### 3.1. Chemical reactions of fuel reforming

As previously mentioned, catalytic fuel reforming is normally performed to produce a hydrogen-rich reformate. Chemical reactions taking place in this complex process are influenced by many factors that include both engineering choices and physical conditions.

The selection of a primary fuel is very important for any engine, more so for an ICE with TCR. In principle, a wide range of energy sources can be used as a primary fuel for reforming. The selection of fuel type for the generation of H<sub>2</sub> takes into account the availability of the primary fuel and fuel supply infrastructure, the energy value of the fuel, the thermal conditions of the reforming process, the reformate composition, the cost of catalysts needed for reforming, and long-term stability [61]. This choice is coupled with the selection of the heat recuperation process. Thus, the subsequent discussion is divided into the following subsections:

- Recuperation by decomposition and SR (in the absence of oxygen). This is probably the most promising approach and we provide a detailed description of the main reactions (Section 3.1.1), operating temperatures and side reactions (Section 3.1.4).
- Partial recuperation by autothermal reforming, where part of the feed undergoes catalytic combustion in presence of oxygen (Section 3.1.2).
- Dry reforming where the exhaust gas is used to reform the feed (Section 3.1.3). This process and to a lesser extent SR, exhibit catalyst deactivation due to coking (Section 3.3).

##### 3.1.1. Main reactions in steam reforming (in the absence of oxygen)

A schematic layout of steam fuel reforming application to an internal combustion engine is displayed in Fig. 2.

Herein, we describe the main factors that affect the choice of fuel, while limiting ourselves to the main reactions [SR, water gas shift (WGS), and decomposition reactions (Eq. 1)] that are inevitable in most systems:

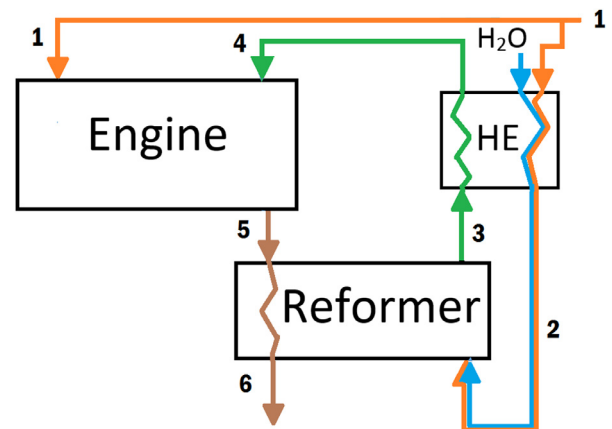
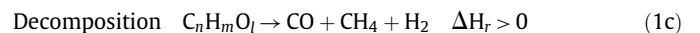
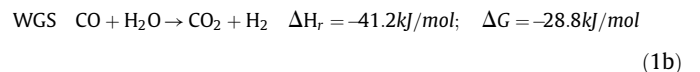
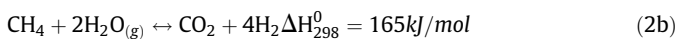
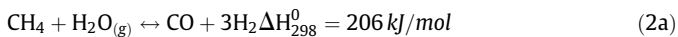


Fig. 2. A scheme of steam fuel reforming in ICE. 1 – primary fuel; 2 – preheated mixture of primary fuel and water; 3 – hot reformate; 4 – cooled reformate; 5 – engine-out exhaust gas; 6 – system-out exhaust gas. HE – heat exchanger.

These are overall (unbalanced) reactions that do not describe the atomistic mechanism and ignore the formation of many other possible products (several specific cases are outlined below). However, for reformer design purposes, most studies present the kinetics in terms of one (overall SR), two (SR, WGS), or the three reactions. Product composition depends on the catalyst and reaction conditions, however, with leading selective catalysts, the selectivity to other products may be small or even negligible. Sufficiently high temperatures, high steam/carbon ratios (S/C), and long residence times lead to syngas (CO + H<sub>2</sub>) that partially undergoes a WGS reaction (Eq. 1b) to form CO<sub>2</sub>. Whether one should aim for sole decomposition (in the absence of steam – Fig. 2) or the overall reaction depends on various factors including the S/C ratio, available heat transfer areas, coking, and reformat feed dependence of ICE behavior.

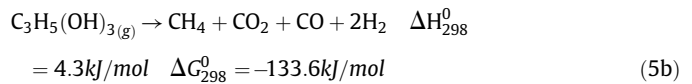
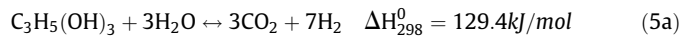
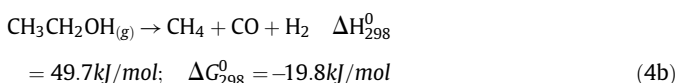
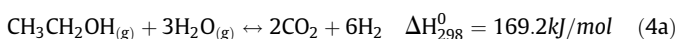
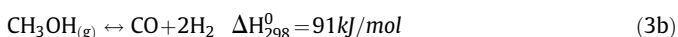
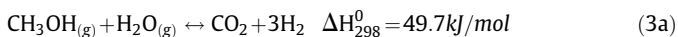
To make the discussion more concrete, the following examples are considered:

**Methane SR:** Natural gas (mainly comprising methane) has captured the attention of researchers as a potential primary fuel for onboard reforming [23,62–64]. Compared to diesel fuel and gasoline, natural gas is a truly low carbon intensity fuel [65]. Moreover, it is normally free from aromatic hydrocarbons, thereby contributing towards lower particle emission [66]. In addition, natural gas reserves are globally more evenly distributed, thus contributing towards energy supply security and more stable market prices [23]. Methane SR is usually described by Eq. 2a, followed by the WGS reaction (Eq. 1b).



Eq. 2b describes the overall system. The reforming temperature of methane is relatively high (723–1023 K) [63,67] and is mainly determined by the equilibrium conditions required for high conversions. Catalyst deactivation caused by the sulfur content in natural gas can also be challenging in onboard fuel reforming [23], however technologies for sulfur removal (desulfurization) are available.

**Alcohol reforming:** The overall steam reforming processes of methanol (MSR), ethanol (ESR) and glycerol (GSR; by-product of biodiesel production) are represented by Eqs. 3a–5a. On the other hand, the kinetic scheme of higher order (C ≥ 2) alcohol reforming involves many possible side reactions, so that other compounds, such as alkenes, aldehydes etc. are produced along with the components of the reaction set. Many studies have reported that when SR is conducted on various catalysts based on Ni, Ir, Co, Ru, Rh, Pt or others, the most significant products are CH<sub>4</sub>, CO<sub>2</sub>, CO and H<sub>2</sub>. These are created by the decomposition of methanol, ethanol, glycerol (Eqs. 3b–5b), and other oxygenates, which are endothermic with negative ΔG values and can be considered irreversible at low pressures. The decomposition is followed by an endothermic SR reaction, an exothermic WGS reaction, dehydrogenation and methanation [68–78]. At the right conditions (temperatures > 573 K, moderate pressures, but mainly high residence times), the conversion of methanol, ethanol and glycerol is complete, as predicted thermodynamically [79].



Methanol decomposition can occur on Cu at temperatures as low as 473 K. Since the subsequent WGS reaction is already active at these temperatures, high MSR conversions can be achieved at low temperatures. Moreover, large temperature gradients can be established for heat transfer in the recuperation process. Ethanol decomposition can proceed at low temperatures but produces methane (as well as syngas). Thermodynamic analysis suggests that to achieve reasonable conversions in the subsequent methane SR reaction (Eq. 2a), temperatures > 873 K are required. The same applies to GSR [80,81]. Evidently, the reformer limiting temperature is that of decomposition and methane can be fed as part of the fuel. Moreover, higher temperatures are required for more complex feeds.

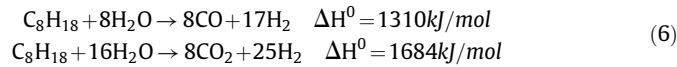
Nowadays, ethanol reforming is still attracting much attention. This process affords a high hydrogen production yield, and with a proper selectivity - low rates of side reactions [82]. The thermodynamics of ESR has been widely discussed in the literature [82–85]. Methods and main findings of the reforming thermodynamic analysis are discussed hereafter (sub-Section 3.2). Attempts to analyze ESR in view of its use in ICE with TCR were made in [45,86]. It was shown, using the equilibrium approach and considering SR, methanation, ethylene formation and polymerization reactions, that the optimal ESR energy efficiency (sub-Section 3.2) and the highest hydrogen yield are achieved at T = 1073 K and a steam-to-ethanol (S/E) ratio of 1.2 (at atmospheric pressure). CH<sub>4</sub> and CO<sub>2</sub> molar fractions reach a minimum at T = 1073 K and S/E = 1.2 and increase with a further rise in the S/E ratio. This S/E value is substantially lower than the one recommended for fuel cell applications (S/E = 3...6) [85,87]. In these latter applications, CO formation must be eliminated via the WGS reaction (Eq. 1b) to avoid the fuel cell electrodes from being poisoned by CO [85]. Conversely, in ICE application, CO does not act as a poison. Thus, compared to fuel cell applications, the S/E ratio required for onboard ESR can be greatly reduced. This implies less energy required for water heating and evaporation. Unfortunately, analysis of the whole ICE-reformer system [86] revealed that high-temperature ethanol steam reforming is not a practical option for ICE with TCR and does not allow final efficiency improvement of the whole engine-reformer system. This is due to the large energy demand of the high-temperature SRE process, which cannot be satisfied without compromising the engine efficiency.

Hence, experimental attempts to reduce the reforming temperature have been made to maximally utilize the engine waste heat [26,88–90]. Hu et al [89] focused on reforming hydrous ethanol (75% ethanol and 25% water) by applying a dielectric barrier discharge plasma reactor filled with quartz beads. A 45% conversion was reported. Shimada & Ishikawa [90] studied SR of hydrous ethanol with 40–60 wt.% ethanol over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst at 573 K reporting relatively low conversion that decreased with a reduction in ethanol concentration (hydrous ethanol). Li et al [26] argued that rich feed is not viable and suggested as optimal S/E = 1 (i.e. 75% hydrous ethanol). They studied ESR over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, using the exhaust gases to heat the reformer, and achieved up to 57% conversion at 673 K that dropped to 27% at 573 K. However, catalyst deactivation due to pulverization and coking was also reported. Morgenstern and Fornango [88] suggested another approach to low-temperature ethanol decomposition (Eq. 4b) at 523–573 K, thus enabling utilization of exhaust waste heat. The method was extensively tested by the authors [27,91,92]. They reported that compared to E85 (reference fuel), 50% fuel reforming led to a substantial increase in BTE (10–17%) at medium and light loads. The pre-ignition problems observed in ICE with TCR were resolved by limiting

the hydrogen content in the induced fuel via partial fuel reforming at light and medium loads and by using the liquid unreformed fuel (E85) at high loads.

Efficient high-pressure fuel reforming plays an important role in realizing the significant advantages of ICE with direct fuel injection. These include a higher maximal power per unit cylinder volume and prevention of pre-ignition problems [13].

**Octane/gasoline reforming:** Due to the difficulty of replacing the existing distribution infrastructure of gasoline, there is vast interest in the reforming of octane. This usually requires high temperatures and was investigated mainly in the context of H<sub>2</sub> and synfuel production for fuel cells (PEM and solid oxide fuel cell - SOFC, respectively). Al-Musa et al. [93] studied isooctane SR on supported Cu catalysts. In the absence of side reactions, the desired reactions (Eq. 6) were predicted to yield H<sub>2</sub> selectivities of 17/25 and 25/33 for S/C ratios of 8 and 16, respectively.



Al-Musa et al. [93] also revealed that high conversion can be achieved at temperatures  $\geq 973$  K and S/C ratio of 24. H<sub>2</sub> selectivity of  $\sim 55\%$  with relatively high selectivity towards methane ( $> 20\%$ ) and several higher alkanes is obtained (Fig. 3). These values should be compared to equilibrium calculations exhibiting  $> 70\%$  selectivity towards H<sub>2</sub> with nil production of methane and other alkanes. The interpretation by Kopasz et al. [94] suggests breakup of isooctane into lighter hydrocarbons, followed by SR, WGS reaction, methanation, and other reactions to produce the observed distribution. The results in Fig. 3 afforded when using a ceria support, are significantly better than those on other supports that exhibit smaller conversions and smaller H<sub>2</sub> selectivities and higher methane concentrations [93]. However, Cu/Ceria catalytic activity deteriorates with time due to coking.

We have elaborated on isooctane SR to demonstrate that: (i) the thermodynamic predictions may be limited, and (ii) SR of octane requires high temperatures that may render recuperation impractical. Still, future discoveries of better catalysts may alter this conclusion.

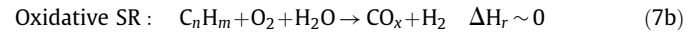
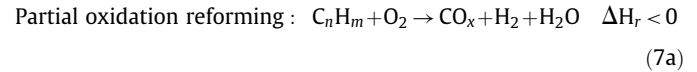
**Other fuels:** Other considered primary fuels for onboard reforming include dimethyl ether (DME) [95], urea/ammonia [96–98], glycerol [81], and liquefied petroleum gas (LPG) [99,100]. Cracknell et al. [101] attempted to formulate synthetic fuels that are compatible with both the reformer and the ICE.

In summary, the reaction temperature should be sufficiently low to allow heating of the feed with the engine exhaust gas at a reasonable heat transfer area. Typical exhaust gas temperatures for SI engines range from 823 and 1073 K, depending on the operation

mode. Conversions at the given reformer temperature may be limited by kinetics or thermodynamics in a reversible reaction. In general, alcohols and oxygenates are more reactive than hydrocarbons [102]. Hence, these alcohols can be reformed at relatively low temperatures by using relatively cheap catalysts. The low reforming temperature for methanol (523 – 573 K) [54,55] and ethanol (573 – 873 K) [55,88,103] (depending on the desired reaction, decomposition or SR) along with sufficient heat transfer between the exhaust gas and the reformer, afford a complete reforming by utilizing only the exhaust gas heat. However, according to thermodynamics, considerable amounts of methane may be produced in ESR. Complete ESR to H<sub>2</sub> and CO<sub>2</sub> requires significantly high temperatures 873 – 1073 K [104,105], which cannot be attained with the reformat as a standalone fuel. High conversion in methane SR requires temperatures  $> 1023$  K. Gasoline and diesel fuel reforming usually requires temperatures  $> 1073$  K. This is considered impractical unless coupled, to some degree, with fuel combustion (Section 3.1.2). Most of these results are limited to atmospheric pressure. An increase in pressure would lead to declining equilibrium conversions with stronger effects at lower temperatures (Fig. 4).

### 3.1.2. Auto-thermal reforming (in the presence of oxygen)

To overcome the endothermicity of SR and coke deposition, several studies introduced a limited amount of oxygen (air) to achieve partial oxidation (Eq. 7a and Fig. 5) or oxidative SR (Eq. 7b and Fig. 6). The latter may allow achieving an energetically near-neutral system.



The above equations are not balanced and exothermicity depends on reaction selectivity to H<sub>2</sub>, which in turn depends on the operating conditions. However, one cannot simply control the product distribution. Hydrogen is usually more reactive to oxidation than alkanes and alcohols and will probably be consumed if oxygen is available. Higher amounts of oxygen in the reactor will allow greater internal heat production through exothermic oxidation reactions, however at the expense of a lower heating value of the resultant reformat.

Partial oxidation reforming (Eq. 7a) may look simpler, because it does not require water as a reactant (Fig. 5). However, its design raises many issues. For example, should the partial oxidation be catalytic? Otherwise the reformer temperature may exceed that of the exhaust. The SR technique affords a larger H<sub>2</sub> yield and a higher reforming product heating value over partial oxidation reforming

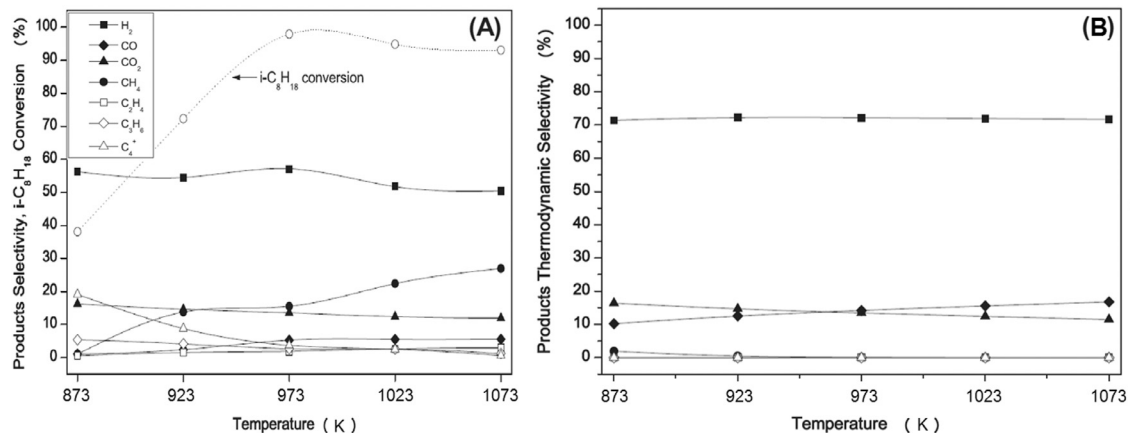


Fig. 3. Effect of temperature on selectivity (A) and on equilibrium composition (B) during isooctane SR on Cu/Ceria (after Al-Musa et al. [93]). Reaction conditions:  $P_{i-\text{C}_8\text{H}_{18}} = 1.5\text{kPa}$ ;  $P_{\text{H}_2\text{O}} = 36\text{kPa}$ ;  $m_{\text{cat}} = 250\text{ mg}$ ;  $F_T = 150\text{ cm}^3/\text{min}$ .

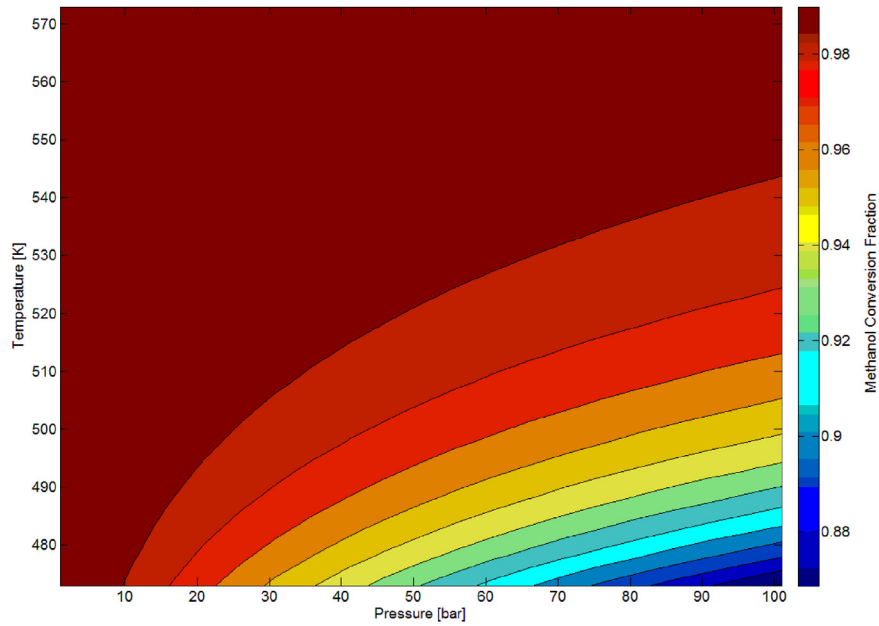


Fig. 4. Influence of reforming pressure and temperature on equilibrium fuel conversion. Primary fuel – methanol, S/M = 1, considered reactions – SR and WGS.

[106]. Oxidative SR (auto-thermal reforming - Eq. 7b), a hybrid process that combines the first two strategies (Fig. 6), enables energetically balancing exothermic partial oxidation and endothermic SR by proper selection of  $O_2/C_nH_m$  and  $H_2O/C_nH_m$  molar ratios [107]. Again, its design raises several questions and optimization problems.

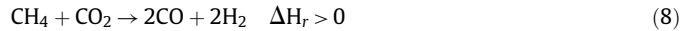
As argued earlier (sub-Section 3.1.1), the high temperatures required for steam reforming of methane and higher hydrocarbon fuels (gasoline and diesel fuel) make this approach unpractical for most applications of ICE with TCR. In this case, partial oxidation (Eq. 7a), where the energy required to sustain the endothermic reactions is supplied through exothermic reactions of fuel oxidation, is more suitable for onboard fuel reforming [108]. The catalysts used to promote partial oxidation reactions should withstand high temperatures [109]. Moreover, they should be resistant to the effects of adsorption of sulfur species originating from the fuel [110] and to the formation of inert carbon-rich species that could block the catalytically active sites [108,111]. However, the use of fuels that undergo hydrodesulfurization is anticipated in future applications.

Partial oxidation can be used with gasoline as a fuel to offer certain advantages for engine startup. However, it requires a specific reformer design, while recuperation of the exhaust energy is

doubtful. This process can afford high CO and  $H_2$  selectivities but only within a narrow parameter domain. Moreover, its product distribution (including some olefins) may lead to coke formation [112].

### 3.1.3. Dry reforming and exhaust gas fuel reforming

Endothermic dry reforming is another possible type of reforming reaction, which is intensively considered by researchers, especially for gasoline and diesel fuel reforming [113,114]. For methane:



Its main advantage is in using exhaust gas for fuel reforming [47,60,108,115]. This method was developed in the past few decades by researchers from the University of Birmingham [113,116]. It relies on achieving energy recovery from hot and wet exhaust gases by endothermic catalytic dry reforming and SR of hydrocarbon fuels with a fraction of the engine exhaust gas (Fig. 7). The presence of oxygen in the exhaust gas also results in exothermic reactions of fuel oxidation. Thus, exhaust gas fuel reforming can be described by the ideal reactions of partial oxidation reforming (Eq. 7a), SR (Eq. 1a), dry reforming (Eq. 8), WGS (Eq. 1b), and complete fuel oxidation. However, Tsolakis and Golunski [117] claimed that there is

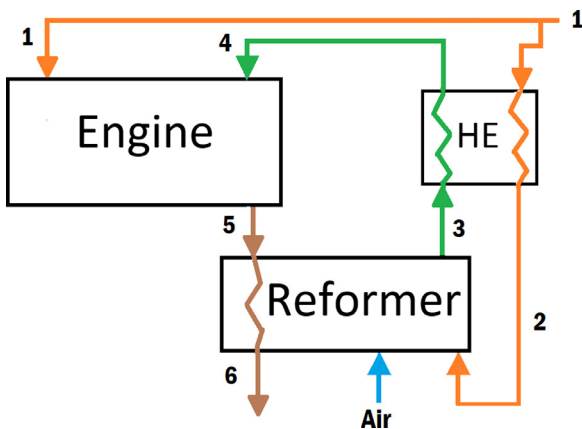


Fig. 5. A scheme of partial oxidation fuel reforming in ICE. 1 – primary fuel; 2 – pre-heated primary fuel; 3 – hot reformat; 4 – cooled reformat; 5 – engine-out exhaust gas; 6 – system-out exhaust gas. HE – heat exchanger.

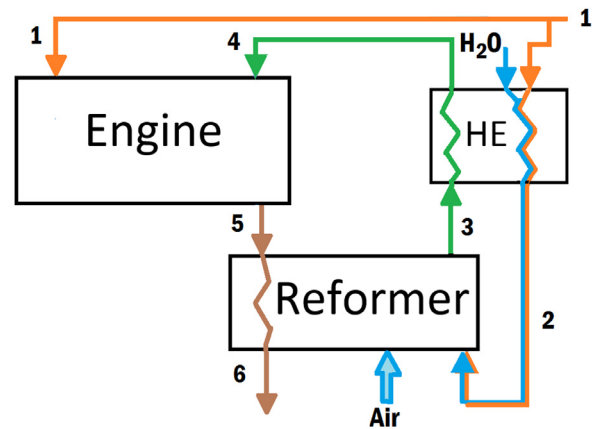
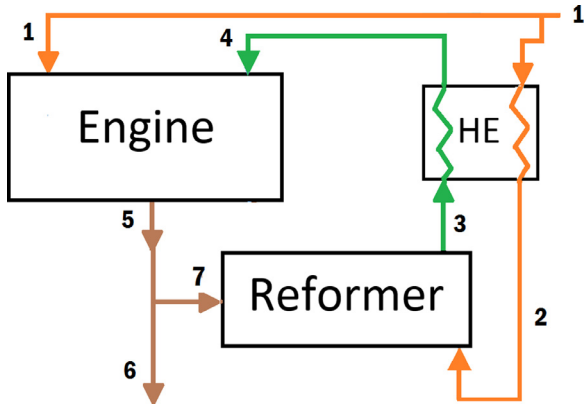


Fig. 6. A scheme of auto-thermal fuel reforming in ICE. 1 – primary fuel; 2 – pre-heated mixture of primary fuel and water; 3 – hot reformat; 4 – cooled reformat; 5 – engine-out exhaust gas; 6 – system-out exhaust gas. HE – heat exchanger.



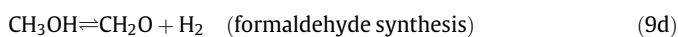
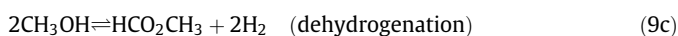
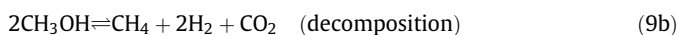
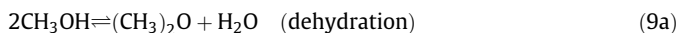
**Fig. 7.** A scheme of exhaust gas fuel reforming in ICE. 1 – primary fuel; 2 – preheated primary fuel; 3 – hot reformed gas; 4 – cooled reformed gas; 5 – engine-out exhaust gas; 6 – system-out exhaust gas; 7 – fraction of exhaust gas participating in the reforming process. HE – heat exchanger.

no conclusive evidence of direct partial oxidation (Eq. 7a) in exhaust gas reforming. High temperatures ( $\geq 1073$  K) are required to sustain exhaust gas fuel reforming reactions [60,118].

The thermodynamic benefit of exhaust gas fuel reforming depends on the dominance of the endothermic reactions of SR (Eq. 1a) and dry reforming (Eq. 8) [115]. In these reactions, a hydrocarbon fuel is converted to a mixture of  $H_2$  and CO (both ICE fuels) by consuming exhaust gas energy. Thus, a gaseous reformed fuel with higher enthalpy than that of the primary fuel is produced. Reactants required to sustain the steam and dry reforming reactions are water and carbon dioxide, both of which are present in engine exhaust gas. As mentioned above, oxygen is also usually present in exhaust gas (especially in diesel engines) and is consumed through complete or partial fuel oxidation reactions. These exothermic oxidation reactions reduce the process efficiency, but are required to raise the reformer temperature. The main disadvantage of this approach is coke formation [47]. Thus, the reforming conditions must be carefully controlled to avoid intensive carbon formation and deposition on the catalyst. The hydrogen-rich reformed gas is usually recirculated into the intake manifold so that the term “reformed exhaust gas recirculation (REGR)” is frequently used [115]. Tsolakis et al. [119] reported a 3% fuel consumption reduction with REGR addition. They also determined that the bioethanol-fueled homogeneous charge compression ignition (HCCI) engine demonstrates higher tolerance to REGR than EGR, thus enabling extension of the HCCI operating mode and a reduction of pressure rise rates due to the higher REGR levels. Lebouvier et al. [120] studied exhaust gas fuel reforming of diesel fuel by a non-thermal arc discharge for  $NO_x$  trap regeneration. This and other applications of fuel reforming for exhaust gas aftertreatment are discussed below in Section 6.

### 3.1.4. Side reactions

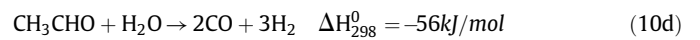
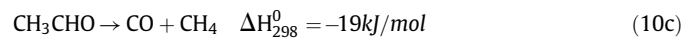
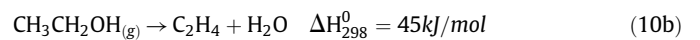
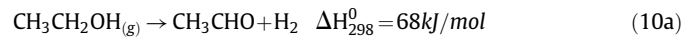
As stated above, several undesired products may be formed during the reforming process. Byproducts, such as dimethyl ether (Eq. 9a), methyl formate (Eq. 9c), and formaldehyde (Eq. 9d) may be formed during methanol decomposition and MSR. These in turn may promote deactivation routes via pyrolysis.



Reactions such as methanation (Eq. 9b) and reverse methane SR (Eq. 1a) are also possible. These reactions can be suppressed by choosing the appropriate catalyst and S/C ratio.

Deactivation by CO disproportionation (Boudouard reaction,  $2CO \rightarrow C + CO_2$ ) is considered less favorable for MSR since the higher  $CO_2/CO$  ratio minimizes the thermodynamic driving force. Changes in oxidation state [Cu(0)/Cu(I)] may also result in decreased activity and changes in selectivity. Twigg & Spencer [121] reported that coking and catalyst poisoning (chloride, sulfur) remain the main sources of deactivation in methanol decomposition and methanol SR reactions involving advanced promoted CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts.

For ESR, aside from the desired reactions (Eq. 4a), several other reactions including ethanol decomposition (Eq. 4b), ethanol dehydrogenation to acetaldehyde (Eq. 10a) and its subsequent decomposition (Eq. 10c) or SR (Eq. 10d), ethylene formation (Eq. 10b), and the Boudouard reaction, may also occur [82,122].



### 3.2. Thermodynamic analysis of the reformer-ICE system

Thermodynamic analysis of fuel reforming is usually performed to evaluate the influence of the reforming process parameters (reactants ratio, temperature, pressure, etc.) on the reformed composition. Thermodynamic analysis of various reforming methods (mainly for  $H_2$  production in fuel cell applications) is quite common [82,123–125]. However, most studies are limited to atmospheric pressure and high S/C ratios. For the analysis, the reactions or the set of species should be specified. The analysis is performed either using equilibrium constants [123,126], or by minimization of Gibbs free energy [82].

As previously discussed, the fuel reforming process is a complex multiple reaction system. The total enthalpy of combustion of the reforming products depends, in a complex manner, on the process conditions. To analyze the efficiency of the fuel reforming process, it is essential to know the integral effect of the process variables on the total enthalpy of combustion of the reforming products and the heat duty (enthalpy of reaction + enthalpy of vaporization + sensible enthalpy). The latter is the invested resource [127]. Based on the 1st law, this efficiency can be defined, as the ratio of the difference between the enthalpy of combustion of the reforming products  $H_{comb}$ , and enthalpy of the primary reactants  $H_{in}$ , to the invested resource - heat duty  $H_d$  (Eq. 11) [45]:

$$\eta = (H_{comb} - H_{in})/H_d \quad (11)$$

In [128] a comparative analysis of energy efficiency of different alcohol reforming processes was performed for various reforming temperature and steam-to-fuel (when relevant) conditions. The maximal reforming efficiencies of the ESR, MSR and low-temperature ethanol reforming (ethanol decomposition) processes were determined at 0.59 ( $T = 1073$  K and steam-to-ethanol ratio = 1.2), 0.66 ( $T \approx 573$  K and steam-to-methanol ratio = 1.2) and 0.42 ( $T = 570$  K, no water added), respectively. The above-discussed approach is sometimes adopted for tasks where an ICE with TCR is considered. In the latter case the reformer and the engine are analyzed separately and outputs of the reforming process investigation are used as inputs for the engine performance analysis and vice versa [86,128].

Clearly, when fuel reforming is employed for waste heat recovery and hydrogen production in ICE, the ICE and the reformer units are coupled and thus, the system should be considered as a whole. This



requires an appropriate modeling approach. Relatively few efforts have been made to perform thermodynamic analysis of a complete system that includes an ICE and a reformer. Information on 2nd law analysis of an ICE with TCR is especially limited. Chakravarthy et al. [20] have performed a detailed 1st and 2nd law thermodynamic analysis of thermochemical recuperation (TCR) applied to an ideal internal combustion engine. They assumed the engine to be operating over an ideal cycle at constant pressure or constant volume gaseous fuel/ air mixing in the combustion chamber, isentropic compression of the air-fuel mixture, adiabatic constant-volume combustion of the mixture at the point of maximum compression, and isentropic expansion of the burned gases to atmospheric pressure. The adiabatic reformer is assumed to reach the equilibrium of the SR reaction (only  $\text{CO} + \text{H}_2$  products). At constant-pressure mixing, primary fuel reforming, reformat cooling and mixing of the cooled reformat with air are performed at constant ambient pressure prior to entering the combustion chamber. For constant-volume mixing, reforming and reformat cooling with subsequent reformat-air mixing are assumed to take place at constant volume. Hence, contrary to the constant-pressure case, the initial pressure in the combustion chamber is higher than the ambient pressure. Notably, in their analysis, Chakravarthy et al. significantly simplified the processes that occur in a real ICE with TCR. Moreover, the authors of [20] considered various fuels and showed that due to an extension of the lean combustion limit, ICE fed by hydrogen and CO yielded more work per unit fuel exergy. They also determined that for a stoichiometric methanol/air mixture, TCR can increase the estimated ideal engine 2nd law efficiency by  $\sim 3\%$  (percent-points) or  $> 5\%$  for constant-pressure or constant-volume reforming, respectively. The better efficiency of the latter process is attributed to the increase in the net expansion work caused by a higher initial cylinder pressure. For ethanol and isooctane, the estimated second law efficiency increase for constant volume reforming is 9 and 11 percent-points, respectively. These results reveal that the 2nd law efficiency improvement observed for TCR is mainly due to the higher inherent exergy of the reformat and the pressure boost associated with an increase in the number of moles of the gaseous reforming products. Evidently, the idealistic simplified approximation of the engine working cycle does not take both the finite duration of fuel combustion and the increase in pumping work due to throttling into consideration. Thus, the important benefits of  $\text{H}_2$ -rich reformat fuels (high burning velocity and wide flammability limits), which enable the system to approach the efficiency of an ideal Otto cycle and unthrottled operation, cannot be assessed. Although this work suggests that ethanol and isooctane SR are viable recuperation vectors (Fig. 8), a single reaction under equilibrium is assumed and temperatures are significantly larger than expected because of the assumed adiabaticity.

The exhaust gas exergy upstream and downstream of a reformer was analyzed to assess exhaust energy recovery in an SI ICE fed by gasoline (primary fuel) with exhaust gas fuel reforming [129]. Exergy analysis allowed the investigation of the influence of the reformed EGR (REGR) flow rate and the reformed fuel fraction on exhaust gas energy recovery. An increasing energy recovery trend (reduction of exhaust gas exergy) with increasing REGR rate and reformed fuel fraction was revealed [129]. Applying 2nd law ICE-TCR system analysis through the exergy destruction approach allows a comparison between various fuel reforming methods and targeting of the system components where most exergy (ability to produce work) is lost. This approach was recently applied by Chuahy & Kokjohn [130] to a CI engine fed by diesel primary fuel and a dual-fuel combustion strategy in which the reformat was employed as a supplement to the primary fuel. A comparison of three different fuel reforming methods (partial oxidation, auto-thermal reforming, and SR) revealed that the highest exergy destruction was afforded for partial oxidation (due to its exothermic nature, while SR provided

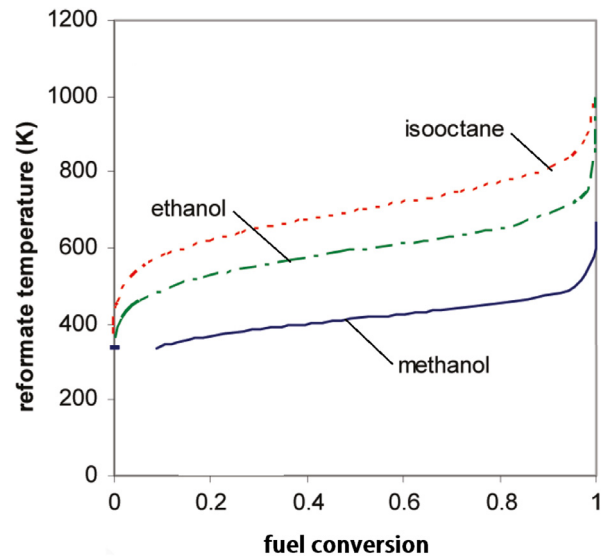


Fig. 8. Effect of a primary fuel on reformat exit temperature – thermodynamic analysis of a reformer-ICE system (note the required temperatures for high conversions), after Chakravarthy et al. [20].

the highest 2nd law efficiency. Notably, the 2nd law analysis performed in this work enabled identifying a substantial exergy destruction source in the investigated TCR system layout – reformat cooling downstream of the reformer. This was responsible for up to 13.6% system exergy destruction of the endothermic reforming systems [130]. To mitigate this exergy loss, primary fuel pre-heating by a hot reformat can be applied [131] (Figs. 2, 5–7).

The inclusion of reforming kinetics into the combined ICE-reformer model is essential to predict reformer size, reforming dynamics, and the mutual relationship of the ICE and reformer performances. A joint engine/reformer operation must be considered to accurately predict the exhaust manifold and reformer effluent conditions. Such a combined model was developed for a DI SI engine with TCR and methanol primary fuel using GT-SUITE software [132] and is described in [133]. A common approach to reformer modeling as a 1-D non-isothermal homogeneous packed bed reactor (no inter-phase gradients were assumed) with co- or counter-current heat exchange was applied. This method allows more flexibility in the choice of catalyst type. An empiric power-law rate equation was used instead of full kinetic-derived schemes.

This model was further developed and applied to the thermodynamic analysis of a direct injection (DI) SI ICE with high-pressure TCR [13] and of a DI HCCI engine with reforming-controlled compression ignition [134]. In the latter case, a single-zone HCCI combustion process was assumed and the combustion rate was predicted based on the chemical kinetics equations suggested by Kaiser et al. [135] (standard ChemKin-II formatted mechanism file). Thermodynamic properties of the species used in the chemical kinetic model were acquired from the ChemKin-II thermodynamic data. These methods of TCR are discussed later in this article (Section 5).

Application of the joint ICE-reformer model with reforming kinetics allows the prediction of the transient behavior of complex ICE-TCR system and the peculiarities of heat transfer phenomena as well as optimization of the reformer design and reformat supply strategy. Moreover, it numerically proves that the contribution towards BTE improvement from lean engine operation (possible because of the  $\text{H}_2$ -rich reformat fuel) is greater than that from the fuel LHV increase [133]. Results of thermodynamic analysis performed using this model revealed that the reformat direct-injection method is unviable when reforming is carried-out under

atmospheric pressure [13]. The significance of cooling the reforming products prior to their injection into the engine-cylinder was demonstrated.

Numerical approaches to reformer or/and engine (fuel-air mixing and combustion) modeling can be applied when detailed information about species flow and concentration fields is required [136–138].

### 3.3. Carbon deposition and S/C effect

Carbon deposition is probably the most important concern that needs to be addressed in all catalytic techniques employed in hydrocarbon and oxygenate fuel reforming, including oxidative reforming [107,111]. Carbon can be formed mainly either through a strongly endothermic hydrocarbon thermal decomposition reaction [139]:



or through associations and polymerization of olefins. This undesired phenomenon is especially relevant when processing heavy fuels, since thermal cracking reactions can easily occur at relatively low temperatures and the formed byproducts (mainly olefins) can induce the formation of carbonaceous deposits [140–142]. Moreover, when alcohols are reformed (e.g. ethanol) in an insufficient steam supply, they can dehydrate to ethylene according to Eq. 10b with subsequent carbon formation through ethylene polymerization [82]:

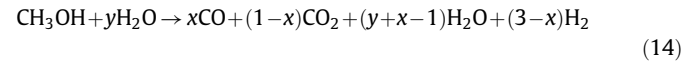


Carbon can also be formed from decomposition or hydrogenolysis (Eq. 9b or 4b and Eq. 13a for methanol and ethanol, respectively) and the subsequent methane decomposition reactions (Eq. 13b), as well as from the Boudouard reaction (Eq. 13c):



The rate of coking crucially depends on the S/C ratio, since the coke can react with surface oxygen produced from water dissociation. Most ICE-with-TCR studies (both experimental and numerical) have naturally focused on methanol as a primary fuel due to its relatively low reforming temperature [25,56,128,143] trying to find an optimal steam-to-methanol (S/M) ratio. In their review, Iulianelli et al. [38] reported that S/M < 1 can provoke coke formation and catalyst deactivation. As a result, most research on MSR has focused on S/M > 1. In their work [144], Choi and Stenger demonstrated that at S/M > 0.76 (mole/mole), the MSR products are limited to CO, CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub> only. While the decomposition reaction is fast and

almost complete, the subsequent WGS reaction is limited by kinetics (low temperatures) or equilibrium (high temperatures). The overall reaction for methanol is:



$$\{ 0 \leq x \leq 1, 0 \leq (y+x-1) \}$$

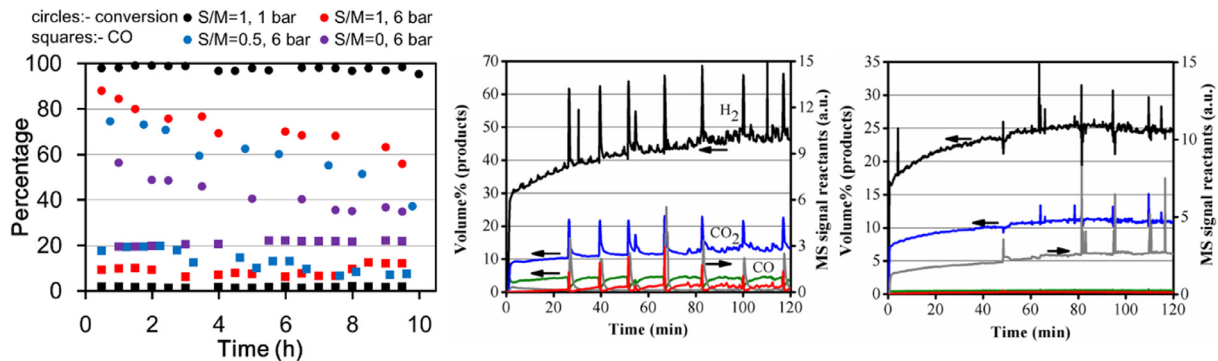
where  $x$  is the CO selectivity [145]. Thus, CO selectivity is the only factor affecting the heating value (HV) of the methanol reformat, and HV increases linearly with  $x$ . Higher S/M ratios lead to a decline in CO formation [146] and therefore, a reduction in reformat heating value. Moreover, the energy necessary for water evaporation requires a larger heat transfer area between the exhaust gas and the methanol-water mixture at the evaporator. A high S/M ratio usually implies a more stable catalyst, however, this effect is not accounted for in most models. Agarwal et al. [147] reported an increase in the MSR reaction rate when the S/M ratio was increased to 1.4, thereby allowing downsizing of the reformer. However, in many cases, the rate is determined by heat transfer. Data reported by Santacesaria & Carrá [148] only agree with the findings of Agarwal et al. at temperatures  $\leq 453$  K. Results afforded by Lee et al. [149] also do not support these findings. These data imply that for an ICE with TCR using methanol as primary fuel, the S/M ratio should be in the range of 1 and 1.4 [133]. Thattarathody et al. [150] studied the kinetics and deactivation of MSR over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> at  $0 < S/M < 1$  and  $P < 6$  bar. They found deactivation rates to be marginal at 1 bar for S/M > 0 but become appreciable at higher P and/or S/M = 0 (Fig. 9). It is attributed to coke formation based on Temperature Programmed Oxidation of spent catalyst. CO concentrations are negligible at S/M = 1 and significant at S/M = 0 and/or high pressure.

Rostrup-Nielsen [152] studied the thermodynamic proclivity of gaseous mixtures to coke formation with subsequent carbon deposition on the catalysts. Equilibrium with respect to SR (Eq. 1a) and WGS (Eq. 1b) reactions was assumed in this work. However, other factors also influence the likelihood of carbon (coke) formation. For example, the nature of the solid catalyst is important both in terms of the metal and support [102] (sub-Section 3.4).

In summary, carbon formation is strongly dependent on the type of hydrocarbon to be reformed, catalyst type, reaction temperature, and O/C and S/C molar ratios. Higher O/C and S/C ratios reduce coke formation.

### 3.4. Reforming kinetics and catalyst selection

Catalysts should be active, selective, stable over time, inexpensive and safe. Activity and selectivity are determined by the active metal choice and sometimes by interaction with the support. Catalysts are usually build with a porous support to provide high surface



**Fig. 9.** Left (after Thattarathody et al. [150]): Dependence of deactivation rate (as evident by conversion vs TOS), and of CO production, on pressure and S/M ratio during MSR on CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> ( $T = 275$  C,  $W/F_{\text{meth}} = 0.025$  kg<sub>cat</sub> s mmol<sup>-1</sup>). Right (after Thattarathody & Sheintuch [151]): Oscillatory behavior evident by MS signals obtained during methanol steam reforming with steam/methanol ratio 1:1 (300 mg catalyst, Ar flow through methanol-water mixed solution - 10 ml/min, center, or 50 ml/min, right).

area, active metals that catalyze the reaction and promoters that are usually added to enhance stability by suppressing coking (carbon deposition) or inhibiting sintering (coalescence of catalyst crystallites), two of the main causes of deactivation. However, the support is not inert and in many cases, it affects deactivation or even reaction rates. Catalyst components are still chosen based on experience and qualitative understanding.

Most of the reported results were conducted with steam at atmospheric pressure and isothermal conditions. Conditions in the actual reformer can be different in an ICE with direct reformat injection, since the reformer must operate at pressures as high as those in the engine cylinder during the compression stroke. Furthermore, decomposition reactions maybe superior to those observed in SR. However, information about deactivation under such conditions is scarce. Catalyst selection and the determination of reaction kinetics still require a lengthy experimental study and cannot be presented as a methodical procedure. Over the past two decades, emerging studies have employed computational catalysis (DFT) for catalyst selection (mainly of active metal) and derivation of kinetics, however, a description of this is beyond the scope of this review.

**Methanol SR:** Two groups of catalysts are employed in methanol SR: copper-based catalysts, which are inexpensive and active and group VIII - X catalysts, which exhibit better thermal and long-term stability. Copper-based catalysts are preferred for economic reasons [54]. However, these catalysts display some disadvantages including pyrophoricity and deactivation by thermal sintering, coke deposition, and changes in oxidation state [144,153,154]. Copper crystallites readily undergo sintering at temperatures > 573 K [121]. Indeed, for conventional copper-based catalysts, an operating temperature ≤ 533 K is recommended. Copper sintering is also reported to be a function of steam concentration.

A detailed review of MSR studies published by Sa et al. [54] lists the active catalysts, supports, promoters, mechanism, and kinetics of the process. When the SR temperature ranges between 473 and 573 K, e.g. when methanol is employed as a primary fuel, SR is favored over the commercially available catalyst - alumina-supported Cu/ZnO [25,56,128]. The CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>-based catalysts have been extensively studied both at low-temperature (453 – 483 K) and higher temperature (473 – 573 K) ranges [121,145,146,155–163]. More importantly, copper-based catalysts are not active in the methanation (reverse reforming) reaction (Eq. 6b) and gas that is almost methane-free can be produced at low temperatures and high pressures to fully convert a primary fuel to CO<sub>2</sub>, CO and H<sub>2</sub>. CuO/ZnO formulations usually comprise stabilizers and promoters, such as alumina, alkaline earth oxides, and other oxides, to inhibit sintering and absorption of catalyst poisons. Table 1 summarizes main recent findings on the most popular copper-based catalysts. Notably, most studies do not employ the S/C = 0 (i.e. decomposition) scenario.

Several studies have focused on the effect of catalyst structure and catalyst synthesis procedures. Zirconia was shown to have a promotional effect on Cu-Zn catalysts by decreasing CO selectivity [167,168]. In addition, ZrO<sub>2</sub> can increase Cu dispersion [167]. Al<sub>2</sub>O<sub>3</sub> can increase both the total surface area and Cu dispersion [168], while Cr<sub>2</sub>O<sub>3</sub> was reported to stabilize Cu against sintering [169,170]. The promotional effects of CeO<sub>2</sub> on Cu proved better than those of a ZnO, Al<sub>2</sub>O<sub>3</sub>, or ZnO-Al<sub>2</sub>O<sub>3</sub> system under the same reaction conditions [171]. This was attributed to the high dispersion of Cu metal particles and strong Cu-CeO<sub>2</sub> interactions. In the mixed oxide catalyst CuZnGaO<sub>x</sub> [165], the interface between Cu metal-defective oxides plays an important role in determining the activity. For the recently developed PdZn/ZnO catalyst [172], a strong synergism between active sites on the PdZn alloy and those on the ZnO support is necessary for excellent catalytic activity. The activity and selectivity are strongly influenced by the calcination atmosphere of the ZnO precursor with increased activity from oxidation to reduction. The increase in the concentration of oxygen vacancies on the surface of the ZnO support increases the activity by providing additional sites for water adsorption. Thus, the replenishment of oxygen vacancies on this support leads to the suppression of CO formation. However, catalyst activity dropped by 24% after a 48-h stability test under MSR conditions. The activity and selectivity of the Pd/ZrO<sub>2</sub>-m (monoclinic) catalyst were further enhanced by the addition of copper as a promoter particularly at low temperature (< 493 K) [166]. The enhanced activity results from the strong interactions between Pd and Cu as well as enhanced metal phase dispersion when monoclinic ZrO<sub>2</sub> was used. Zn/TiO<sub>2</sub> catalysts were also considered for methanol reforming [173]. Pinzari et al. [173] reported that an adequate amount of zinc ( $\chi_{Zn} > 0.02$ ) in the catalyst is necessary to prevent coke formation and reduce the formation of undesirable byproducts. Pd-based catalysts are also receiving much attention due to their high activity and selectivity [174,175].

Several studies have correlated measured data to a reaction rate expression, usually presented as a single reaction. Initial attempts described the kinetics by power law rate expressions. Jiang et al. [176] analyzed the reaction mechanism of MSR on Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>. They employed the Langmuir-Hinshelwood rate equation, assuming that the r-WGS reaction is negligible. Peppley et al. [160,161] developed a comprehensive model for the kinetics of MSR on Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts from the analysis of the surface mechanism; this accounted for all three possible overall reactions. Certain questions about process modeling, such as whether the process comprises decomposition and WGS (Eqns. 3b, 1b) or overall SR and r-WGS (3a, reverse 1b), remain open. At high contact times and temperatures, the WGS (Eq. 1b) reaches equilibrium with the result being independent of the route. Under other conditions, the predicted CO/CO<sub>2</sub> ratio is dependent on the assumed mechanism. Thattarathody et al. [150] studied the kinetics and diffusion effects of MSR over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> at 0 < S/M < 1 and P < 6 bar in a packed-bed for application as

**Table 1**  
Catalyst performance for MSR.

Catalyst	T(C), (1atm)	S/C	Main results (M = CH <sub>3</sub> OH; W = H <sub>2</sub> O)
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> (Sud-Chemie) [144]	110–360	0–1.75	Reduction of methyl formate, DME and methane upon addition of H <sub>2</sub> O
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> (3 Sud-Chemie and 1 Syntex) [164]	180–270	1.4	Above 230 °C, all catalysts exhibited similar activities with methanol conversion > 90%
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> (Sud-Chemie) [145]	230–300	1	Full conversion achieved at W/F > 0.01 and at T > 250 °C.
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> (syntex 33–5) [149]	160–260	1–2	Reaction rate depends on P <sub>M</sub> and P <sub>H<sub>2</sub></sub> , and not on P <sub>CO</sub> , P <sub>CO<sub>2</sub></sub> , P <sub>W</sub> .
Cu/Zn/Al <sub>2</sub> O <sub>3</sub> (with Cr or Zr promoter) [158]	180–320	1; in N <sub>2</sub>	Higher Cu content leads to higher conversion and selectivity.
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> (Sud-Chemie) [146]	175–350	1.3	Appreciable concentration of CO at low contact times and high conversions (S/C = 1), suppressed by increased S/C ratio.
Cu/ZnO/Ga <sub>2</sub> O <sub>3</sub> [165]	150–195	2	Lower T and shorter contact time reduces the CO level, trend opposite to CuZnO <sub>x</sub> -based catalyst
CuPd/ZrO <sub>2</sub> -m [166]	< 220	1.5	Enhanced activity and selectivity particularly at low temperature (< 220 °C)
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> [150,151]	< 300C	0–1	Faster deactivation at 6 bar and/or S/M = 0 or 0.5, suppressed rate under these conditions, possible oscillatory behavior

**Table 2**

Ethanol steam reforming at 973 K under stoichiometric reaction conditions ( $n(\text{H}_2\text{O})=3$ ,  $n(\text{C}_2\text{H}_5\text{OH})=1$ ) at atmospheric pressure on  $\gamma\text{-Al}_2\text{O}_3$  supported Rh, Pt, Pd, Ru, Ni, Cu, Zn and Fe catalysts [177].

	Gas phase composition (%)						H <sub>2</sub> yield (g h <sup>-1</sup> g <sup>-1</sup> catalyst)	Selectivity towards CO <sub>2</sub> (%)
	H <sub>2</sub>	CO <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>		
Thermodynamic equilibrium	69.2	10	20	0.8	0	0	–	33
1%Rh/ $\gamma\text{-Al}_2\text{O}_3$	72	21	7	0	0	0	2.3	75
1%Pt/ $\gamma\text{-Al}_2\text{O}_3$	46	7	13	12	21	1	0.6	35
0.75%Pd/ $\gamma\text{-Al}_2\text{O}_3$	55	2	18	15	9	1	1.1	10
0.67%Ru/ $\gamma\text{-Al}_2\text{O}_3$	38	2	9	12	38	1	0.3	18
9.7%Ni/ $\gamma\text{-Al}_2\text{O}_3$	70.5	18	11	0.5	0	0	3.1	62
9.1%Cu/ $\gamma\text{-Al}_2\text{O}_3$	40	1	12	21	23	1	0.4	8
9.8%Zn/ $\gamma\text{-Al}_2\text{O}_3$	42	0	16	21	20	1	0.4	0
8.7%Fe/ $\gamma\text{-Al}_2\text{O}_3$	44	5	10	20	20	1	0.3	33

the feeding reformat to ICE utilizing TCR. A simple kinetic model assuming methanol decomposition followed by WGS was used to describe the results and its parameters calibrated ( $E_a = 50$  kJ/mole, independent of S/M). At atmospheric pressure, conversions at S/M=0 were inhibited (Fig. 9), probably due to CO inhibition. The apparent methanol decomposition rate constant ( $k_{MD}$ ) is almost diffusion-free for a 0.7-mm particle size. Analysis and experiments suggest that 1–2 mm pellets are optimal.

Evidently, the kinetics can be significantly more complex than the models described above. A parallel study [151] using an AutoChem Micromeritics 2920 micro-reactor reported oscillatory behavior evident by MS signals observed at 523 K (Fig. 9, right). A complex model is necessary to account for this behavior, however, such a model is not expected to change the recuperation properties of the system significantly.

**Ethanol SR:** A comparative study of product distribution on various catalysts at 973 K, atmospheric pressure and stoichiometric feed was presented by Aupretre et al. [177]. This suggested the following order in terms of hydrogen yield: Rh~Ni > Pd > Pt > Cu~Zn > Ru (Table 2). Note that Rh and Ni also produce little ethylene (a coke precursor) and methane.

Catalysts based on Ni, Cu and Co active phases supported on zirconia, alumina, and magnesia are frequently used for ethanol steam reforming [122]. There is rich evidence to suggest that Ni-based catalysts are often prone to coke deposition [178,179]. Ni/La catalysts have also displayed high activity in ethanol reformation and improved stability at increased temperatures and high S/C ratios [180]. Resini et al. [181] have studied Ni–Zn–Al- and Ni–Mg–Al-based catalysts for ethanol steam reforming and only observed H<sub>2</sub>, CO<sub>2</sub>, CO, and CH<sub>4</sub> in the products at temperatures  $\geq 750$  K. Under these conditions, the H<sub>2</sub>-yield is limited by the fast WGS reaction that reaches equilibrium. At lower temperatures, the yield is also limited by the ESR equilibrium [181]. Furtado et al. [182] reported that applying 1% Cu and 10% Ni on ceria/zirconia resulted in a substantial improvement of catalyst activity. Goula et al. [183] studied ESR over a Pd/ $\gamma\text{-Al}_2\text{O}_3$  catalyst to afford a hydrogen selectivity up to 95% at ~923 K. They observed an increase in coke formation when water-to-ethanol ratio in the feed stream decreased below the stoichiometric value; this was well in agreement with works that investigated MSR. Promising results were achieved by Benito et al. [122]. They found that Co-based catalyst supported on zirconia displays high resistance to coke formation and excellent stability. In addition, complete ethanol conversion was achieved at temperatures  $\geq 873$  K. Morgenstern and Fornango [88] developed a novel Raney-type Ni-Cu catalyst (sponge-metal catalyst, porous structure with a large surface area) from Raney nickel coated with a high loading of copper (28%). In the absence of water, high ethanol decomposition activity was achieved at temperatures typical for MSR (523–573 K). Such low reforming temperatures enable the use of ethanol reforming in ICE with TCR, when all the energy required to sustain the

endothermic reaction of ethanol decomposition can be recovered from the engine exhaust gas [27].

Catalysts comprising more than one active species have also been investigated because of their significantly different catalytic properties with respect to either of the parent metals [184,185]. The synergistic effect of Pt addition to Ni-based catalysts improved the activity of the non-noble metal towards hydrogenation reactions to afford lower coke formation rates than those observed for monometallic Ni-catalysts [184]. When Pt and Ni were supported on CeO<sub>2</sub> by depositing the non-noble metal on the support surface before the noble metal, Pt became directly available at the gas-solid interface and ethanol adsorption was favored. Thus, better agreement with thermodynamic data from a regular fixed bed was observed [74,103]. Zhong et al. [186] reported that Rh/ZrO<sub>2</sub> and Rh-Fe, and Rh-Co/Ca are good catalysts for ESR. They demonstrated that Fe<sub>x</sub>O<sub>y</sub> incorporation reduces CO adsorption on Rh by CO spillover and subsequent WGS on Fe [187].

**Hydrocarbons SR:** More expensive noble metal-based catalysts are usually required for hydrocarbon fuels reforming due to poisoning (by sulfur) and coking (Section 3.1.2). Amongst the catalysts aimed at onboard hydrocarbon fuel reforming, Pt–Rh-based catalysts supported on ceria-zirconia, K-promoted Co–Rh catalysts, and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts are frequently considered [188–190]. Peucheret et al. [190] reported that a slightly less active but less sulfur-sensitive catalyst can be designed by using a more sulfur-tolerant support material and excluding Pt (oxidizes SO<sub>2</sub> in the exhaust to SO<sub>3</sub>). They concluded that the Pt–Rh catalyst is most suited to exhaust-gas fuel reforming in engines fed with a sulfur-free fuel, whereas the Rh-only catalyst is the better choice when the fuel contains sulfur. Nickel has also been considered as a catalyst for gasoline fuel reforming (mainly for fuel cell applications) because of its high electronic conductivity, thermal stability, activity, and low cost [191]. However, it presented low conversion of gasoline-type fuels at low temperatures typical for modern ICEs (especially for diesel engines) and was easily deactivated at high temperatures [192–194]. Addition of a second metal (Co, Mo, W, Re, or Pd) to the Ni-alumina catalyst resulted in some activity improvement at lower operating temperatures [195].

### 3.5. Reformate gas constituents

H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub> and H<sub>2</sub>O are the main products of fuel reforming (unreformed fuel usually presents in the reforming products as well). In oxidation reforming, N<sub>2</sub> and O<sub>2</sub> can be found in the final reformat. Knowing the physical properties of various reformat components is essential to assess the physical properties of the reformat mixture. Table 3 lists various properties of the main reformat constituents as well those of the most common primary fuels for comparison.

The parameters that influence the composition of the reforming products include the primary fuel type, reforming method, steam-

**Table 3**  
Properties of main reformat constituents and primary fuels [23,24,56,60,134,196–208].

Parameter	H <sub>2</sub>	CO	CH <sub>4</sub>	DME	C <sub>2</sub> H <sub>6</sub> O	CO <sub>2</sub>	H <sub>2</sub> O liquid	Gasoline	Diesel fuel	Methanol	Ethanol
Molecular weight (kg/kmol)	2.016	28.01	16.04	46.07	44.01	18.02	~ 111	170	32.04	46.07	
Density (kg/m <sup>3</sup> ) @ 1 bar & 298K	0.08	1.14	0.65	0.67	1.977	1000	750	830	792	789	
Boiling point (K) @ 1 bar	20	81.5	112	249	194.7	373	303–463	453–633	338	351.3	
Mass diffusivity in air (m <sup>2</sup> ·10 <sup>-4</sup> /s)	0.78	0.19	0.16	n/a	0.14	0.24	0.07	0.0463	0.14	0.11	
Minimum ignition energy (J·10 <sup>-3</sup> )	0.02	0.23	0.28	0.045	–	–	0.24	0.23	0.215	0.65	
Minimum quenching distance (m·10 <sup>-3</sup> )	0.64	3.2	1.9–2.03	n/a	–	–	2.84	2.1	1.8	~1.65	
Flammability limits in air (vol %)	4–75	12.5–74.6	5.1–15	3.4–18.6	–	–	1.5–7.6	0.6–6.5	6.7–36	3.3–19	
Stoichiometric air-to-fuel ratio (kg/kg)	34.2	2.467	17.1	9.0	–	–	14.7	14.6	6.47	9	
Lower heating value (J·10 <sup>6</sup> /kg)	120	10.1	50	27.6	–	–	44	43	20	26.9	
Volumetric energy density (J·10 <sup>6</sup> /m <sup>3</sup> ) @ 288 K, 1 bar	10.3	12.6	33.4	19,300	–	–	33,750	35,800	15,840	20,900	
Laminar flame speed (m/s) @ λ = 1, 1 bar, 298K	2.07	0.165	0.36	0.43	–	–	0.30–0.50	0.22–0.25	0.43	0.41	
Autoignition temperature (K) @ 1 bar	858	882	813	508	–	–	530	523	743	636	
Adiabatic flame temperature (K) @ λ = 1, 1 bar	2318	2223	2230	n/a	–	–	2470	2200	2194	2050	
RON	n/a	106	120	n/a	–	–	95–98	n/a	106	108	

\* n/a – not available

to-fuel ratio, reforming temperature and catalyst selectivity [54]. The highest hydrogen yield (up to 75 mol % H<sub>2</sub>) is achieved with MSR (Eq. 3a) and ESR when other reactions are ignored. A very high reformat hydrogen content results in higher values of burning velocity and wider flammability limits (Table 3). Reduction in the steam-to-fuel ratio contributes towards a decrease in the H<sub>2</sub> fraction and to the replacement of CO<sub>2</sub> with CO. For example, the use of a nickel-based catalyst can contribute towards the formation of CH<sub>4</sub> for both methanol and ethanol reforming [54]. When methane is formed during the reforming process, whether intentionally or as a byproduct, the reformat volumetric energy density increases (Table 3), while the hydrogen content decreases, thus affecting the burning velocity and flammability limits of the reformat.

### 3.6. Reformat combustion

Information on the fundamental combustion properties (mainly combustion front velocity) of the reforming products is essential for a comprehensive analysis of the ICE-TCR system, as well as for the design of a dedicated combustion chamber. Data on the dependence of the laminar burning velocity on pressure, temperature, mixture composition, and stretch rate are essential for engine combustion models.

An acceptable approximation for laminar burning velocity ( $S_L$ ) was suggested by Frank Kamenetskii [209]:

$$S_L = (k(T_m)D)^{1/2} \quad (15)$$

where  $k(T_m)$  is the first-order reaction rate constant estimated at the maximal temperature ( $T_m$ ), usually from the Arrhenius relation;  $k = A \exp(-E/RT)$ ; and  $D$  is the diffusivity that exhibits  $D \sim 1/P$  behavior.

Numerous studies of the burning velocities of pure H<sub>2</sub> and some syngas (H<sub>2</sub>/CO) mixtures were reported [210–212]. Verhelst and Wallner [196] have compiled a detailed overview of hydrogen combustion in internal combustion engines along with relevant information on phenomena leading to hydrogen flame cellularity (flame front instability), laminar and turbulent burning velocities at atmospheric conditions (Fig. 10) and the effects of various factors on the flame speed in engine-relevant conditions.

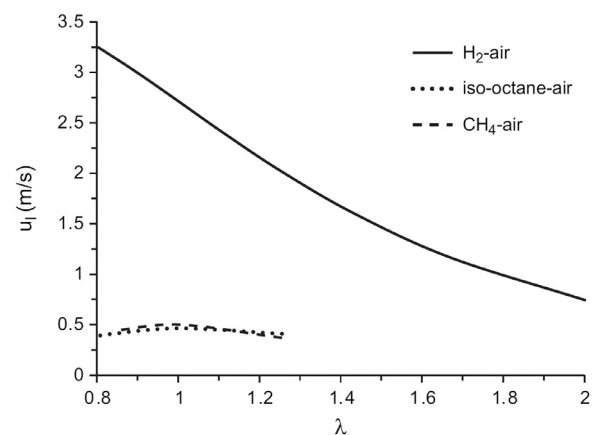
In summary, Verhelst & Wallner [196] have pointed out that experimental data on the laminar burning velocity of H<sub>2</sub>-air mixtures at engine-relevant conditions are still rare and consequently, available numerical data are non-validated. A comparison of data on laminar burning velocity of alcohol reformates (Fig. 11) with those of unreformed methanol and ethanol (Table 3) clearly shows a great advantage of burning H<sub>2</sub>-rich reformates. For example, burning velocity of MSR products containing 75% mol. H<sub>2</sub> and 25% mol. CO<sub>2</sub> ( $x = 0$  and  $z = 0$  point on Fig. 11) at stoichiometric conditions ( $\lambda = 1.0$ ) is well above 1.30 m/sec as compared to 0.43 and 0.41 m/sec

(Table 3) for unreformed methanol and ethanol, respectively. As mentioned previously, higher burning velocity of the fuel in ICE, enables getting closer to the most efficient ideal Otto cycle with heat supply at a constant volume.

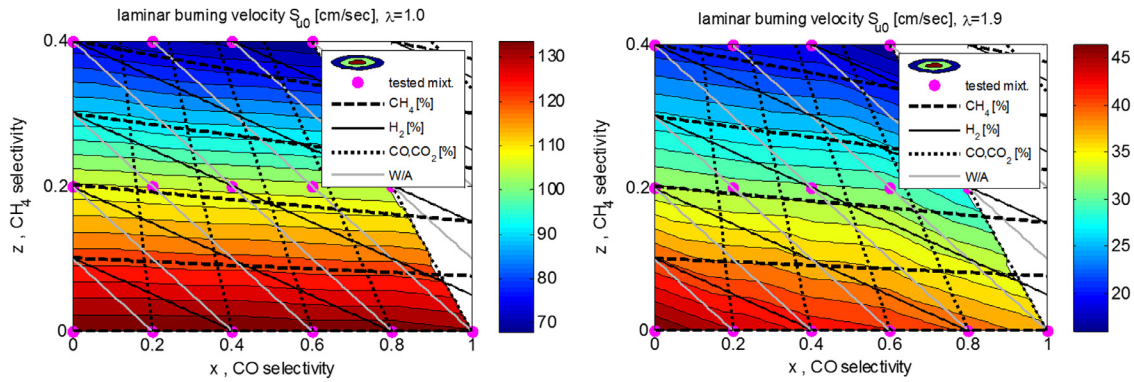
Note that reformat mixtures can be substantially different compared to syngas and vary widely in composition. For example, MSR products consist mainly of H<sub>2</sub> (75% mol) and CO<sub>2</sub> (25% mol), whereas ethanol decomposition products comprise even molar fractions of H<sub>2</sub>, CO and CH<sub>4</sub>. Available data on reformat combustion is fragmentary and not well-systematized. Thus, information on reformates burning velocity and its dependence on reformat composition and combustion conditions is clearly essential.

Poran et al. [133], and Tartakovsky et al. [28,128] simulated reformer-ICE systems operating at different reformat compositions applying the Wiebe model with correction for combustion velocity and reported strong performance improvement with H<sub>2</sub>-rich ICE feed.

Some data is available on the laminar burning velocities of syngas/air premixed flames with varying H<sub>2</sub>/CO ratios (5/95 - 75/25) diluted with N<sub>2</sub> or CO<sub>2</sub> (dilution rate from 0% to 60%) at atmospheric pressure and room temperature at various fuel/air ratios [213]. Notably, presence of a diluent gas, (nitrogen or carbon dioxide), in the reformat leads to a reduction in flame temperature and consequently a decrease in burning velocity. The latter is proportional to the heat capacity of the diluent gas (multiple of its mass and specific heat). The effect of pressure on the burning velocity of some syngas compositions was also investigated in [214,215] for a limited



**Fig. 10.** Laminar burning velocities for hydrogen-, iso-octane- and methane-air mixtures, at 1 bar and ~360 K, as a function of the excess air factor. Reprinted from Verhelst and Wallner (2009) [196] with permission from Elsevier.



**Fig. 11.** Laminar burning velocity of various alcohol reformat compositions at different fuel-air ratios, after Omari et al. [216]. The isolines show constant  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{CO}$  selectivities, as well as constant water-to-alcohol (W/A) ratios. Assumption of full conversion. Color scaled velocity in cm/sec.

pressure range (from 1 to 10 bar). Shy et al. [214] correlated experimental measurements of turbulent burning velocities ( $S_T$ ) of syngas ( $\text{H}_2/\text{CO}$ ) spherical flames with constant turbulent Reynolds numbers and suggested the power-law relation:

$$S_T/u' = a Da^b \quad (16)$$

where  $Da = (L_I/u')(S_L/\delta_F)$  is the turbulent Damköhler number,  $\delta_F \approx \alpha/S_L$  is the laminar flame thickness,  $S_L$  – is the laminar burning velocity,  $u'$  – is the r.m.s. turbulent fluctuation velocity,  $L_I$  – is the integral length scale of turbulence and  $\alpha$  – is the thermal diffusivity of unburned mixture. The values for coefficient  $a$  (0.52) and exponent  $b$  (0.25) were suggested in [214] for a lean  $\text{H}_2/\text{CO}$  flame with a Lewis number  $Le \approx 0.76$ . The expression Eq. 16 was experimentally validated by the authors at a pressure range of 1–10 bar. Goswami et al. [215] studied the influence of elevated pressure (in the same range  $\leq 10$  bar) on the laminar burning velocity of one specific syngas composition (85% vol  $\text{H}_2$ , 15% vol  $\text{CO}$ ).

An experimental study on the effect of reformat composition on the laminar burning velocity at atmospheric conditions was performed by Omari et al. [216] for a wide range of possible reformat compositions that included various  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  contents and for various fuel-air ratios (excess air factor  $\lambda$  ranging from 1.0 to 1.9). Fig. 11 [216] shows that regardless  $\text{CH}_4$  selectivity ( $z$  values), the laminar burning velocity of the reformat decreases slightly with rise of  $\text{CO}$  selectivity ( $x$  values). A stronger reduction in burning velocity with  $x$  increase is observed for leaner fuel-air mixtures.

A decrease in  $\text{H}_2$ -content contributes towards the reduction in laminar burning velocity. Replacement of  $\text{CO}_2$  with  $\text{CO}$  leads to a reduction in the dilution of the fuel-air mixture with  $\text{CO}_2$  and hence, to an increase in the laminar burning velocity. Both factors compete to control the laminar burning velocity, however, due to the significantly higher laminar burning velocity of hydrogen, the  $\text{H}_2$ -content is dominant. This results in a monotonic reduction in reformat laminar burning velocity with increasing  $\text{CO}$  selectivity. This trend becomes stronger for higher excess air factors because of weakening of the  $\text{CO}_2$ -dilution effect in the initially air-diluted mixture.

An increase in methane content in the reformat, i.e. the rise of  $\text{CH}_4$  selectivity ( $z$  values in Fig. 11), leads to a strong reduction in laminar burning velocity. Although the increase in  $\text{CH}_4$  selectivity at constant  $\text{CO}$  selectivity is associated with a simultaneous rise in  $\text{CH}_4$  content and a reduction in  $\text{H}_2$  content, the latter is not the dominant factor that leads to the reduction of the reformat laminar burning velocity. An analysis of the increase in  $z$  along a  $\text{H}_2$  constant-fraction line helps to confirm this statement (Fig. 11). A similar decrease in laminar burning velocity is afforded in both cases ( $z$  increase at  $x$  = constant and  $z$  increase at  $\text{H}_2$ -content = constant). This proves that the increase in reformat  $\text{CH}_4$  content is mainly responsible for the reduction in reformat laminar burning velocity.

Notably, the results discussed above are afforded at atmospheric conditions. Among the few works attempting to address the influence of factors typical for reformat combustion in ICE, the recent study of Nguyen & Verhelst [143] who developed laminar burning velocity correlations over a wide range of ICE-relevant fuel-air equivalence ratios (0.5 – 1.5), temperatures (550 – 800 K), pressures (10 – 85 bar) and EGR levels (0% – 30% mass) are worth mentioning. Varga et al. [217] suggested a joint hydrogen and syngas combustion model based on available experimental data on hydrogen and syngas combustion. This data claimed to cover a wide range of temperatures, pressures, equivalence ratios, and C/H ratios. Moreover, new recommended rate parameters together with their covariance matrix and the temperature-dependent uncertainty ranges of the optimized rate coefficients were provided. The optimized model was compared to 19 recent hydrogen and syngas combustion mechanisms and provides an acceptable reproduction of the experimental data [217].

Simulation of the flame structure and propagation of the premixed laminar flame fronts allows investigation of the knock tendency in spark-ignition engines fed by reformat-enriched fuels. Nguyen & Verhelst [29] applied this approach to methanol-reformat addition over a wide range of dilution levels and unburned gas temperatures and proved that reformat addition, when ICE operates in a dual-fuel mode, reduces the knock tendency. A detailed analysis of knock phenomena in a spark-ignition engine, including super-knock in highly-boosted ICE, with deep insights into the processes occurring during knocking combustion can be found in the recent review of Zhi et al. [218].

#### 4. Design of fuel reformer

Correct design of a fuel reformer is critical for achieving maximal primary fuel conversion, the desired composition of the reforming products, efficient utilization of the exhaust gas energy, low back pressure and negligible coke formation together with compact design and acceptable cost. We review the advantages and shortcomings of popular catalytic reactors like the fixed beds, monoliths and fiber packed beds.

Many fuel reformer designs are based on fixed-bed reactors [26,27,63] that are simple to build and operate. However, fixed-beds are not vibration-resistant and undergo mechanical attrition with time [35]. Another important drawback of the fixed-bed reactors is the relatively large pressure drop. On the other hand, solid-gas heat- and mass transfer, are good. Monolith reactors, which are widely used in exhaust gas aftertreatment systems, are characterized by a low pressure drop and structure robustness [219]. Thus, they have attracted much interest for their potential for application to hydrogen generation [220–223]. The monolith reactor can also be

constructed as a reactor-heat exchanger with a large surface area. One drawback is the laminar flow in the monolith channels, which results in poor (inter-phase) solid-gas mass- and heat transfer. On the other hand, the wall heat transfer and the radial conductivity are better in the monolith compared to the fixed-bed reactor. Novel types of heat-conducting substrates have been recently developed, notably compressed Ni-Al foam, Fe-Cr-Alloy foil, and Cr-Al-O micro-channel cermets [222]. These advancements contribute towards intensifying heat transfer in monolith-type fuel reformers, thus improving their attractiveness for application to ICEs with TCR.

A substantial part of the energy necessary for the reforming process is consumed in the vaporization step. This often goes unnoticed but should be addressed in the system design [35]. In their work, Pettersson & Westerholm [35] overviewed various fuel reformers for fuel cell applications and addressed the main challenges in the reformer design, some of which are relevant for ICE thermochemical recuperation systems. The issue of reactant mixing (e.g., ethanol and water) was stressed by Kumar et al. [224] and much later by Li et al. [26] in their works on the development of a reformer for an ICE fueled by hydrous ethanol. Kumar et al. [224] suggested injecting methanol and water to the reformer via an ultrasonic nozzle, which generated a fine spray of 20- $\mu\text{m}$  droplets. Li et al. [26] designed a special mixing chamber in the reformer to improve gaseous steam and ethanol premixing and to ensure subsequent homogenous catalytic reactions according to the expected water-to-ethanol ratio. Dams et al. [225] have described a reactor made of aluminum with a plate-and-fin heat exchanger design. After oxidation of the aluminum surface, the thin washcoat layer was applied directly on the reactor material. This approach resulted in favorable heat transfer characteristics, the most important feature in ICE-based TCR systems which utilize the waste heat from the engine exhaust gas.

Sall et al. [27] developed and tested three different reformer design versions for low-temperature ethanol reforming (ethanol decomposition; Eq. 4b) intended for automotive applications. They demonstrated that the best catalyst retention and heat-transfer properties are afforded by embedding the catalyst into a fibrous metal basis with a density gradient. The longitudinal shell-and-tube finned tube reformer exhibited efficient heat transfer and acceptable ethanol conversion but proved unsuitable for automotive applications because of its high thermal mass, catalyst settling, and an unacceptable rise in backpressure. The authors suggested a novel transverse shell-and-tube reformer design, where banks of parallel vertical catalyst tubes are extended through a transverse stack of exhaust-side heat-exchange plates. This reformer exhibited high ethanol conversion [27]. Moreover, it featured a relatively low thermal mass and demonstrated a low and stable fuel-side pressure throughout a 500-h test.

## 5. Engines with thermochemical recuperation

Various types of engines with thermochemical recuperation were built and theoretically studied throughout decades of research in this field [26,56,59,80,226]. Most works on alcohol (mainly ethanol and methanol) reforming consider the application of TCR to spark ignition engines [13,25–27,56,90]. Exhaust gas and in-cylinder fuel reforming processes can be efficiently applied to both SI and CI engines [60,108,115,119,227–229]. Shudo et al. [230,231] suggested and experimentally studied an HCCI engine where thermochemical recuperation was applied to both waste heat utilization and control of the combustion process. Their approach is based on reactivity-controlled compression ignition [232,233], which requires in-cylinder burning of two different fuels. This method utilizes DME and hydrogen-containing methanol decomposition products as high- and low-reactivity fuels, respectively. The main advantages of this concept include the need for only one fuel tank with liquid methanol as a primary fuel and improved energy efficiency. The latter is

achieved by exhaust heat utilization to sustain the endothermic reactions of methanol dehydration to DME (Eq. 9a) and decomposition to syngas (Eq. 3b) [231]:



However, the method utilizing on-board production of DME and syngas from primary methanol requires two separate reactors, which complicates the fuel supply system. Furthermore, the application of methanol thermal decomposition for syngas production (Eq. 3b) exhibits an increased rate of coke formation [153] (section 3.7) that may result in catalyst deactivation, thereby slowing down or even terminating the process.

Another method that employs reforming-controlled homogeneous charge compression ignition was suggested and theoretically proven by Eyal & Tartakovsky [134]. The main difference from the method reported by Shudo et al. is the application of only one reformer to control the production of both DME and  $\text{H}_2$ .

The common finding in all studies on SI and CI TCR ICEs is that the achievable improvement in energy efficiency is generally proportional to the hydrogen content of the reformato combusted in the engine cylinders. Evidently, the  $\text{CO}-\text{CO}_2-\text{CH}_4$  balance in the reforming products affects both engine performance and emissions. A high burning velocity and wide hydrogen flammability limits afford the closer approach to the efficiency of the most efficient ideal Otto cycle, and achieve a reduction in cycle-to-cycle variability together with possibility of unthrottled engine operation. Lean burning, possible due to the wide flammability limits of hydrogen, also allows reduction in heat transfer losses and mitigation of pollutant formation. Maximal efficiency gains can be achieved when the ICE is fed with a fuel reformato as a standalone fuel. Recent data of [234] illustrate the experimentally measured benefits of combusting MSR and ethanol low-temperature reforming (ethanol decomposition) products in a direct injection single-cylinder SI engine. The high burning velocity of MSR and ethanol decomposition reformates resulted in significantly lower flame development angles (compared to the gasoline baseline), which was reflected in the reduction in cycle-to-cycle variability. The results of experiments demonstrated that the high hydrogen content in the MSR reformato (75% mol.  $\text{H}_2$ ) allows the engine to operate with acceptable cycle-to-cycle variability [coefficient of variation (COV) < 5%] up to  $\lambda = 3.4$ . The engine was able to run unthrottled at idle at  $\lambda = 7$  as opposed to the lean flammability limit of unreformed methanol at  $\lambda = 1.81$  [235]. Lean burning of  $\text{H}_2$ -rich fuels allows substantial reduction of  $\text{NO}_x$  formation. When a hydrogen-rich reformato is used as a standalone fuel for ICE, dramatic reduction in pollutant emissions together with substantial improvement in energy efficiency is possible. For example, reductions in  $\text{NO}_x$ , CO, HC, and  $\text{CO}_2$  emissions by 73–94%, 90–96%, 85–97%, and 10–25%, respectively, were measured in a DI single-cylinder ICE fed by MSR products (Fig. 12) [131]. Notably, a relatively significant  $\text{CO}_2$  content ( $\leq 25\%$  mol.) in the MSR reformato works as

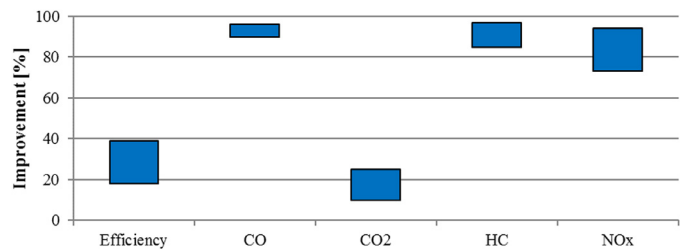


Fig. 12. Improvement in engine efficiency and pollutants emission for MSR reformato feeding compared with gasoline. Single-cylinder DI SI engine, speed 2800 rpm, injection pressure 40 bar, start of injection 127 CAD BTDC, after Poran & Tartakovsky [131].

an inherent EGR and enables NO<sub>x</sub> emission reduction, even at higher loads. The thermal efficiency of the DI engine fed by MSR products improved by 18–39% over engine operation with gasoline (Fig. 12). As previously mentioned, this improvement is a result of the joint influence of the following factors:

- Higher burning velocity of the hydrogen-rich MSR reformate. This affords the closer approach to the efficiency of the most efficient ideal Otto cycle (heat supply at constant volume).
- Wider flammability limits of the hydrogen-rich MSR reformate. This allows unthrottled ICE operation in the whole range of studied engine loads. Thus, a more significant improvement in efficiency was observed at lower engine loads.
- Fuel-air mixture dilution with excess air and carbon dioxide (an inherent component of the MSR reformate). This resulted in lower temperatures in the combustion chamber and as a result, lower heat losses.
- Waste heat recovery, which resulted in a higher MSR reformate heating value.

Notably, the percentage efficiency improvement (18–39%) over ICE feeding with gasoline is higher than the reduction in CO<sub>2</sub> emissions (10–25%) because of carbon redistribution from CO and HC emissions to CO<sub>2</sub>. For ICE feeding with gasoline, the carbon supplied with the fuel is emitted as CO<sub>2</sub>, CO, and unburned hydrocarbons (HC). On the other hand, for ICE feeding with MSR products as a standalone fuel, emissions of CO and HC are mitigated by 90–96% and 85–97%, respectively (Fig. 12). Hence, almost all the carbon introduced by the fuel into the ICE is emitted as CO<sub>2</sub>, thereby resulting in lower reduction in CO<sub>2</sub> emissions relative to efficiency improvement. The results reported in these two works [131,234] give an indication of the good potential of high-pressure TCR application in achieving a substantial reduction in pollutant emissions without aftertreatment. However, because the experiments reported in these studies were conducted at constant speed, it is too early to indicate whether exhaust gas aftertreatment would be necessary at an automotive scale. Should exhaust gas aftertreatment be required, a catalytic converter should be placed upstream of the reformer. In such a configuration, cold start performance of the aftertreatment system would not be affected and no significant influence on the TCR performance is predicted.

Cold start and transient behavior of engines with TCR were identified as a major drawback of this concept [56,59]. Combustion of a primary fuel has been considered as a tool for enabling ICE-with-TCR cold starting and quick regime changing, thus leading to dual-fuel engine operation with subsequent limitations of burning primary fuels [56]. Some new approaches to address the startup and transient operation challenges have been recently suggested. Shudo et al. [231] proposed the use of two accumulation vessels that allow HCCI operation in a wide range of engine loads and speeds. Consequently, the system weight and volume are increased, which may be critical in some applications. Tartakovsky et al. [45,128] suggested integrating an engine with TCR into a series-type hybrid propulsion system, thus ensuring ICE operation at a constant regime favorable for TCR, with the possibility of a reformer startup through electric heating. The main disadvantage of this approach is the need for a more complex design with all inherent disadvantages of a series hybrid propulsion. Notably, an ICE with TCR integrated into a series hybrid propulsion has not been reported to date.

In summary, nowadays, research and engineering aimed at developing an ICE with TCR is attracting much attention. Promising improvements in efficiency and emission mitigation have been demonstrated. However, market implementation of this technology is still remote. Reformer design should aim towards the development of compact, reliable, and durable systems. Applying the TCR concept to modern high-performance engines will require further

advancement in adaptive control strategies. Further research is required to resolve the startup and transient behavior challenges and bring the ICE-with-TCR concept to a market-ready development level.

## 6. Fuel reforming for emission aftertreatment systems

The positive effect of hydrogen on engine performance and emissions has been well documented [196,236] and is discussed briefly in this article. Moreover, when applied directly, hydrogen addition positively affects the performance of various aftertreatment devices, including catalytic converters, diesel particle filters (DPF), and NO<sub>x</sub> traps [237,238]. The addition of hydrogen into the exhaust gas, upstream of the selective catalytic reduction (SCR) catalyst in the presence of unburned or injected HCs is known to improve low-temperature NO<sub>x</sub> conversion by preventing catalyst poison accumulation [239–241]. There is also general agreement over the positive effect of hydrogen on activating various hydrocarbons and on the overall rate of HC-SCR NO<sub>x</sub> reduction [241–243]. In their study, Sitshebo et al. [241] revealed that during HC-selective catalytic reduction of NO<sub>x</sub> over silver–alumina, the known promoting effect of H<sub>2</sub> is sensitive to the engine exhaust gas temperature, H<sub>2</sub> concentration, HC concentration, HC/NO<sub>x</sub> ratio, and space velocity.

Hemmings & Megaritis [238] studied the effect of a H<sub>2</sub>/CO mixture at varying ratios on the diesel particle filter regeneration process, whereas syngas was produced onboard through diesel fuel exhaust gas reforming. They revealed that the most effective DPF regeneration is achieved when syngas comprising 60% H<sub>2</sub> and 40% CO is supplied to the filter inlet. The addition of a H<sub>2</sub>/CO mixture resulted in the complete afterburning of methane, ethylene, propylene, and acetylene. At the same time, an increase in NO<sub>x</sub> concentrations was observed after the filter. Gill et al. [244] investigated the influence of the reformed EGR on soot loading in DPF and catalyzed DPF. They demonstrated that the reforming products introduced along the EGR into the engine intake manifold contributed towards the improvement of both engine combustion and aftertreatment system performance. A significant decrease in total engine-out NO<sub>x</sub> emissions together with an increase in both NO<sub>2</sub> concentration and NO<sub>2</sub>/NO<sub>x</sub> ratio was also observed. This resulted in improved filter efficiency and overall soot loading reduction attributed to enhanced soot oxidation through the NO<sub>2</sub>-oxidation mechanism. Soot loading reduction leads to a lower pressure drop on DPF, which is an important filter performance parameter affecting its durability and engine efficiency. Evidently, the application of fuel reforming to improve the performance of emission aftertreatment systems leads to a more complex emission control system, increase in weight and volume (due to addition of a catalytic reformer), and hence, a rise in the cost of production.

Most frequently, the reformate intended to improve the performance of exhaust aftertreatment devices is produced onboard by using catalytic exhaust gas fuel reforming (Section 3.1.3) [237,238,241,244]. However, other approaches based on the application of non-thermal plasma for fuel reforming, aimed at supplying hydrogen to exhaust aftertreatment systems, have also been developed [120,245,246]. Plasma-based reformers can be combined with catalysts, as was suggested by MIT researchers [245,246]. This allows reduction in the required amount of catalytic materials. When noble metals are applied as catalysts, cost savings could be significant. An important advantage of plasma-reforming as compared to its catalytic counterparts, is its rapid startup and transient response [245]. The main challenges are electrode erosion and high electrical power consumption. For example, according to results reported by Lebouvier et al. [120], when considering real NO<sub>x</sub> trap regeneration behavior, the power necessary to run the plasma during the regeneration phase (~12 sec every 11 km), is estimated at 2.2% of the engine



power. Clearly, further reductions in power consumption together with performance improvements are required.

## 7. In-cylinder reforming

In-cylinder fuel reforming is another method of onboard hydrogen production in internal combustion engines [227–229]. The main benefit of this approach is the possibility of using the available engine hardware and elimination of the need for a fuel reformer.

In-cylinder reforming is usually based on one of two basic approaches: (i) burning a rich fuel-air mixture in the engine cylinder to produce partial fuel oxidation products (mainly  $H_2$  and  $CO$ ) and their subsequent addition to a fresh charge and further combustion [227]; (ii) use of a catalytic coating accompanied by water injection to promote in-cylinder fuel SR [228]. Nickel-based catalysts, such as  $Ni/MgAl_2O_4$  and  $Ni/ZrO_2$  have been considered as coatings for the combustion chamber surfaces [228]. Results from the theoretical analysis performed by Sher & Sher [228], suggest the possibility of improving the thermodynamic efficiency of the ideal ICE (compression ratio 25:1) with the in-cylinder fuel SR by nine percent-points (from 66 to 75%).

To achieve partial fuel oxidation, some researchers suggest the use of a dedicated cylinder in which rich-burn combustion occurs. Researchers of the Southwest Research Institute (SwRI) [227] suggested a dedicated exhaust gas recirculation (D-EGR) concept based on this principle, where one cylinder out of four was a dedicated EGR cylinder, providing a constant 25% EGR to the engine – Fig. 13.

Hydrogen presence in EGR contributes towards a higher burning rate and as a result, better EGR tolerance of the engine. Notably, the engine operation stability can decline when a dedicated cylinder is used for reformat production [247]. This is a result of the indicated mean effective pressure (IMEP) discrepancy between the cylinder with fuel reforming and the rest of the engine cylinders. Such a discrepancy can be reduced when a fuel with higher burning velocity and wider flammability limits is applied [247]. The D-EGR concept was proven to work efficiently with different primary fuels such as gasoline, methane, ethanol, and methanol [248–252]. SwRI researchers converted a 2012 Buick Regal GS car engine to D-EGR operation [248]. They demonstrated an improvement in brake

thermal efficiency of at least 10% across the engine performance map. This was attributed to improvement in EGR tolerance and combustion quality. Avoiding the need of a reformer allowed the maintenance of a good ICE transient response. Application of the D-EGR concept allows improvement of the ICE antiknock performance. According to recently reported results [249], an increase in ICE knock resistance is linearly proportional to the fuel reformation ratio and the slope of this improvement is not fuel-dependent. According to this work, a 10% increase in overfueling in the dedicated cylinder (amount of a primary fuel devoted to reforming) equaled a 1.8-point increase in the fuel antiknock index.

Partial fuel reforming can be also achieved through fuel injection during the period of negative valve overlap (NVO) at  $O_2$ -deficient conditions and results in reforming products containing significant levels of  $H_2$  and  $CO$  [253]. Notably, a dedicated cylinder is not required for hydrogen production. NVO-reforming is a kinetically controlled process. Concentrations of the in-cylinder reforming products strongly depend on the fuel injection timing and injected fuel type, however, they exhibit weak changes with NVO duration and initial temperature variations [253]. Thus, NVO-reforming can also serve as a tool for controlled variation of the fuel-air mixture reactivity in low-temperature combustion processes. Moreover, the NVO-generated reformat can improve the main-combustion-period reactivity through both chemical and thermal effects, although significant heat losses during the NVO-period reduce the total-cycle thermal efficiency of the engine [254]. Thermal barrier coatings can be applied to reduce these losses [255]. Acetylene was found to exhibit the largest impact on increasing the fuel-air mixture reactivity for various tested fuels due to its strong relative impact on reactivity and high concentration in the reforming products [254].

Another approach of in-cylinder fuel reforming based on partial fuel oxidation was suggested by researchers from the University of Duisburg-Essen and investigated in cooperation with Karlsruhe Institute of Technology [256–259]. They applied an ICE as a polygeneration source producing syngas (a base chemical), heat and mechanical work in a single device. Polygeneration is not intended for automotive use, but can be beneficial in a variety of industrial applications, for example in the chemical industry [256].

In summary, the biggest advantages of the in-cylinder reforming approach are the avoidance of a catalytic reformer and the inherently good transient and startup behavior. This facilitates its implementation into engine production technologies. Despite a lower potential of in-cylinder reforming in onboard hydrogen production over reactor-involved fuel reforming approaches, significant improvement in fuel economy and emission reduction can be achieved. For example, recent data from D-EGR concept testing in a 2012 Buick Regal over FTP-75 and HWFET driving cycles displayed a fuel economy improvement of 13% and 9% for city and highway driving, respectively, accompanied by a significant reduction in  $NO_x$  emissions (85% in FTP cycle) [250].

## 8. Decisions to be made when considering fuel reforming for ICE

As evident from the abovementioned information, the choice of the primary fuel and reforming method is not straightforward and depends on several factors. The main reforming approaches are:

- **Decomposition:** This approach can be conducted with alcohols at low temperatures but not with low alkanes and requires high temperatures for high alkanes. It is likely to lead to deactivation due to coking (decomposition-to-carbon technology suffers from very fast catalyst deactivation [260]). It does not require energy investment for water evaporation or onboard water storage, moreover, the resulting reformat displays a higher enthalpy of combustion compared to SR.

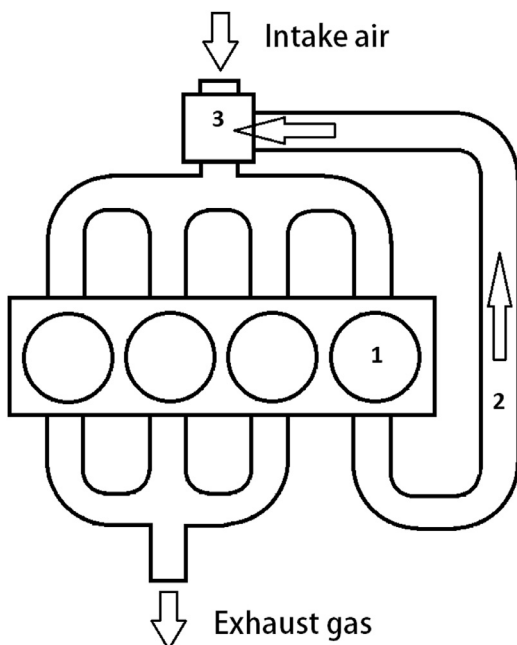


Fig. 13. A schematic layout of the D-EGR concept, after Alger & Mangold [227]. 1 – D-EGR cylinder; 2 – Hydrogen-rich reformat; 3 – Mixer.

- Steam Reforming: This approach can be applied to methanol (and maybe ethanol) at relatively low temperatures but requires high temperatures for octanes. It is less susceptible to coking but requires energy for water evaporation as well as water storage.
- Partial oxidation (or autothermal reforming): This approach is achieved by introducing air to the feed to reach the desired feed enthalpy. This avoids coking but reduces the degree of recuperation.
- Exhaust gas reforming: This approach requires high catalyst bed temperatures ( $> 1000$  K) to allow heat recovery and is also limited by coke formation. However, compared to autothermal reforming, it increases the potential for recuperation due to the presence of both steam and dry reforming reactions. It also enables convenient reforming of conventional motor fuels. Gasoline-fed SI engines are well-suited for exhaust gas reforming because of the high temperature and low oxygen content of the exhaust gas.

The range of ICE operating modes in which the system is only fed by the reformat is a very important issue that influences the trade-off between system complexity and efficiency gain. Evidently, at lower loads, a high  $H_2$ -content fuel would be beneficial because of the wide flammability limits and high burning velocity of  $H_2$ . This makes unthrottled engine operation with a lean fuel-air mixture possible. At high-load regimes it is debatable whether  $H_2$ -rich reformates should be used alone or in combination with a primary fuel to increase the volumetric energy density of the fuel. The latter method could allow downsizing of the reformer-ICE system, improving its transient behavior and providing high peak power. On the other hand, engine feeding with just the reformat at higher loads has the benefit of waste heat recovery through the reforming process. Significant  $CO_2$  concentrations in the reformat at high-load operating modes would allow efficient mitigation of  $NO_x$  formation, thus preventing or at least relieving a need for EGR and other  $NO_x$  emission reduction strategies. The low volumetric energy density of the reformat could be addressed by enhancing methane formation in the reforming process [216].

The selection of an appropriate fuel reforming approach for an ICE requires a number of considerations:

- Whether a catalytic reformer can be applied.
- Type of ICE considered for fuel reforming application.
- Type of primary fuel.
- Whether the reformat will be employed as a standalone fuel or as an additive to be burned together with a primary non-reformed fuel.
- The main purpose of fuel reforming: improvement of ICE efficiency versus improvement of exhaust aftertreatment system performance.

Other factors must also be considered. For example, when considering an alcohol as a possible primary fuel, one is faced with issues of fueling infrastructure, suitability of onboard fuel storage system, etc. Depending on the engine load control strategy, the reformat can be used as a standalone fuel for power output production or as a supplement fuel in a dual-fuel ICE intended for engine performance improvement or/and power production in part of the engine operating range.

Based on the reforming fundamentals (Section 3) and engineering aspects of fuel reforming application in ICEs (Sections 4–7) discussed earlier, in this section we summarize and analyze factors which mutual relationship should be taken into account when considering fuel reforming for ICE.

### 8.1. Considering whether a catalytic reformer can be applied

A variety of reasons may inhibit the use of a catalytic reformer. In such cases, various types of in-cylinder reforming processes should be considered. Clearly, the complete elimination of a reformer to produce a powertrain system of lower weight and size is desirable.

The incorporation of a catalytic reformer imposes additional challenges in terms of powertrain startup and transient behavior. This may limit the range of possible applications and will require appropriate engineering solutions. These include engine startup with a non-reformed primary fuel (with consequent efficiency and especially emission penalties), onboard reformat storage (weight and size penalty), and integration of an ICE with TCR into a series hybrid propulsion system (complexity penalty) [45,59]. Notably, for in-cylinder reforming, the startup and transient behavior problems inherent for reformer-containing applications are eliminated. On the other hand, application of in-cylinder reforming does not allow the maximal possible onboard hydrogen production potential to be reached. This is because only a part of the primary fuel is replaced by the hydrogen-containing reformat and subsequently combusted in the ICE. The application of an in-cylinder catalytic coating [228] raises concerns on catalyst stability that should also be taken into account.

### 8.2. Primary fuel selection

The type of primary fuel determines the possible fuel reforming approaches (Table 4). The distribution of conventional fuels (gasoline and diesel fuel) is simple and relies on the current fueling infrastructure. However, such infrastructure is incompatible with ICE-reformer systems that employ fuels like ethanol and methanol. The chemistry of a fuel (or fuel mixture) in an ICE combustion chamber affects the 1st and 2nd law thermodynamic efficiencies of the ICE through a number of factors. These include the influence of the molar expansion ratio (MER) – a molar ratio of combustion reaction products versus reactants, reaction product dissociation, and specific heat ratio ( $k$ ) [261]. Szybist et al. [261] demonstrated that 1st law efficiency is mainly affected by MER and the  $k$  values of the reactants, whereas 2nd law efficiency is greatly affected by product dissociation.

When adding a reformer to the powertrain system is a viable option, the type of combustion process in the ICE, for which fuel reforming is considered, naturally affects the spectrum of available primary fuels to be considered. However, theoretically, the type of combustion process does not preclude the use of a high-reactivity primary fuel (e.g. diesel and jet fuel) in a spark-ignition engine with fuel reforming. In the latter case, adding a hydrogen-containing reformat to the combustion reaction can improve antiknock stability, as is well documented in literature [262].

When conventional fossil oil-derived fuels are the only options that can be considered, the use of fuel reforming is normally restricted to produce hydrogen as an additive to a primary non-reformed fuel (dual-fuel operation) or a tool for improving the performance of exhaust aftertreatment systems (Section 6). This is mainly attributed to the high temperature required to sustain the endothermic reactions of steam- and dry reforming of gasoline and diesel fuel ( $> 873$  K; Table 4). Thus, in this case, auto-thermal reforming (Section 3.1.2) or exhaust gas fuel reforming (Section 3.1.3) should be employed. Notably, higher amounts of oxygen in the reactor will allow greater internal heat production through exothermic oxidation reactions, however, this occurs at the expense of a lower heating value of the resulting reformat.

Using low-carbon-intensity alternative fuels, like methanol and ethanol, offers much higher flexibility in fuel reforming. The substantially lower reforming temperature (523–573 K; Table 4) enables full substitution of a primary fuel by a hydrogen-rich reformat

**Table 4**  
Main factors affecting fuel reforming for various primary fuels [108,120,129,260,263,264].

Primary fuel	Reforming reaction	Enthalpy of reaction @ 298 K and 1 bar, kJ/mol	Temperature of reforming <sup>a</sup> , K	Likelihood of coke formation	Preferred catalysts	Catalyst cost
Gasoline	Steam reforming	1259 [129]	973–1073	High	Pt-Pd-based Ni-based	High Affordable
	Decomposition	~36 to methane, propene, butane	> 873	Very high	Fe, Ni-based	Affordable
Diesel fuel	Auto-thermal reforming	–	> 973	High	C-based Pt-based	Affordable High
	Dry reforming	1588 [129]	> 973 [108]	High	Pt-Rh based	High
	Steam reforming	1780 [120]	1023–1173 [264]	High	Pt-Pd-based	High
	Decomposition	–	> 873	Very high	Fe, Ni-based	Affordable
Methane	Auto-thermal reforming	–	> 1023	High	C-based Pt-based	Affordable High
	Dry reforming	2887 [120]	> 1073	High	Pt-Pd-based	High
	Steam reforming	165	723–1023		Ni-based	Affordable
	Decomposition	75.6 [260]	773–973	Very high <sup>c</sup>	Ni-based	Affordable
Methanol	Auto-thermal reforming	–	973–1073	Moderate	Ni-based Rh-based	Affordable High
	Dry reforming [263]	247	> 923	High	Ni-based	Affordable
	Steam reforming	50	523–573	Low at S/E > 1	Cu-based	Low
Ethanol	Decomposition	91	473–523	High	Cu-based	Low
	Steam reforming	169	873–1073 <sup>b</sup>	Low at S/E > 3	Noble metals-based	High
	Decomposition	50	~573	Low [88]	Ni-based	Affordable
	Auto-thermal reforming [206]	–	673–773	Moderate	Ni-based Noble metals-based	Affordable High
	Dry reforming [265]	297 [108]	1073–1123	High	Ni-based Pt-Rh based	Affordable High
				High	Co-Rh based	

<sup>a</sup> For maximal hydrogen production;

<sup>b</sup> Lower reforming temperatures result in lower conversion rates;

<sup>c</sup> Faster catalyst deactivation at higher reforming temperature [260]

or the use of reformat gas as a hydrogen additive source. Engine feeding with a reformat as a standalone fuel allows maximal benefits in terms of efficiency improvement and emission reduction. On the other hand, the dual-fuel approach enables downsizing of the system. The choice of partial versus full substitution of the primary fuel by a reformat will subsequently influence the selection of the reforming method, preferred strategy of reformat supply to the engine cylinders, and the possibility of unthrottled engine operation (affects possible efficiency and emission gains). For example, Nguyen & Verhelst [143] have performed a comparative analysis of MSR and exhaust gas reforming methods in the dual-fuel operation of an SI engine with methanol as a primary fuel. They concluded that for the considered conditions, exhaust gas fuel reforming could be beneficial. Clearly, if reforming is considered as a tool to improve the performance of an exhaust aftertreatment system, partial fuel reforming will be sufficient with the consequent flexibility in choosing a primary fuel and a reformat supply strategy.

### 8.3. Strategies of reformat supply to ICE

In earlier versions of ICEs with TCR the reformat was usually supplied to the engine via fumigation into the intake manifold of the engine [56]. Nowadays, diverse strategies of reformat supply to ICE are available. The selection of a specific strategy depends on the reforming application and load control method.

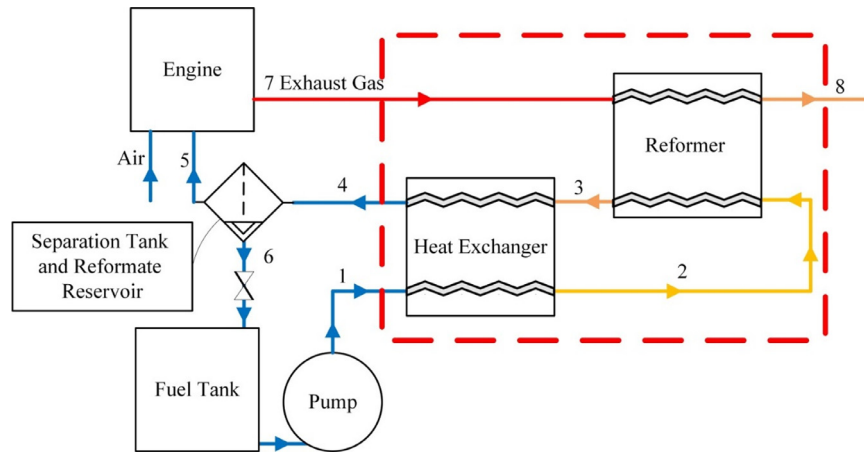
The following methods of reformat supply to ICE are considered [59,202,266]:

- Fumigation into the intake manifold
- Low-pressure injection into the intake manifold or exhaust gas upstream of the catalytic converter/particle filter (depending on reforming application)
- Direct injection into the engine cylinders

Reformat fumigation into the intake manifold is still very popular and is the simplest method of reformat supply. However, this strategy poses several limitations such as backfire and pre-ignition phenomena, and maximal power loss due to the high volume of hydrogen-rich gaseous reformates [59]. Due to the relatively low volumetric energy density, a higher volume of reformat is required for the engine to afford the same power. When the reformat is supplied through the intake manifold, the gaseous fuel replaces the air. Thus, at maximal loads, supplying the required amount of energy with a gaseous reformat will result in subsequent reduction of air mass being ingested by the cylinder, and maximal power reduction. The same results are achieved when a lower amount of gaseous reformat is supplied to ensure its complete combustion. In addition, when the fumigation strategy is applied, the reformat flow rate depends on both the reformat pressure and the instantaneous pressure in the intake manifold. Thus, a decline in fuel flow control accuracy is observed. To mitigate some of these disadvantages, pressure stabilizing valves and flame arresters are frequently installed in the reformat line and intake manifold (between the intake valve and the reformat supply point), respectively [26,266].

In some works, electronically controlled low-pressure injectors have been applied to ensure accurate control of the flow rate at which the reformat is supplied to the engine [23,266]. However, this strategy does not resolve the problems of power loss, backfire, and pre-ignition.

Some studies have attempted to resolve the pre-ignition problem by limiting the hydrogen content in the induced fuel [92]. This was achieved by partial fuel reforming at light and medium loads and the use of an unreformed primary fuel at high loads. Notably, if the pre-ignition problems of ICE operating with a stoichiometric air-reformat mixture and fuel supply to the intake manifold or port fuel injection would be resolved, its maximal power output would still be substantially lower than that observed for a gasoline-fed



**Fig. 14.** Schematic layout of the high-pressure TCR system. 1 – methanol and water mix (1:1 molar ratio) at high pressure; 2 – preheated methanol and water mix; 3 – hot reforming products with residues of unreformed methanol and water; 4 – cooled reforming products with condensed unreformed methanol and water; 5 – cooled gaseous reformate; 6 – condensed unreformed methanol and water; 7 – hot exhaust gas; 8 – cooled exhaust gas. After Poran & Tartakovsky [131].

engine of the same-size. This is a result of the high partial volume of hydrogen in the intake mixture (hydrogen substitutes air in the fresh charge) and absence of charge cooling that takes place during liquid fuel evaporation in the intake manifold.

Using direct injection (DI) as the reformate supply method can solve the above-mentioned problems. Previous studies on CNG- and hydrogen-fueled engines confirmed that DI of a gaseous fuel is the most promising method to achieve high efficiency and a power density comparable to that of gasoline engines, while resolving the pre-ignition and backfire problems [267,268]. For direct injection of gaseous fuel, a relatively high injection pressure is required for two main reasons: firstly, to enable fuel injection late in the compression stroke thereby allowing mixture stratification. Secondly, to limit the increase in compression work caused by the higher partial volume of gaseous fuel compared to its liquid-fuel counterpart. Retarded injection of the gaseous fuel may relieve this negative influence, however, it presumes high injection pressure to overcome the pressure build-up in the engine cylinder. Increased fuel penetration into the densely-charged cylinder and choked flow through the injector (simplifies the fuel flow-rate control) are additional advantages of high-pressure injection of a gaseous fuel [13]. These benefits suggest its suitability for application to an ICE with TCR [128]. Reformate DI eliminates some of the major TCR disadvantages (pre-ignition, backfire, and maximal power loss) without limiting the hydrogen content of the reformate or injecting a liquid non-reformed primary fuel at high engine loads. Of course, the main benefit of DI, namely prevention of engine power loss, is only relevant when the reformate is applied as a standalone fuel for power output production. Contrary to engines fed by a gaseous fuel from the compressed-gas vessels (CNG), in fuel reforming, the energy necessary to compress onboard-generated fuel prior to direct injection must also be taken into account. Poran & Tartakovsky [13] reported that DI-ICE with thermochemical recuperation is unviable if reforming is carried out at atmospheric pressure. Researchers from the Technion suggested a concept of high-pressure thermochemical recuperation based on compression of the liquid primary fuel-water mixture prior to its evaporation. This would significantly reduce energy investment in reformate compression and thus, makes direct reformate injection feasible (Fig. 14) [13,269].

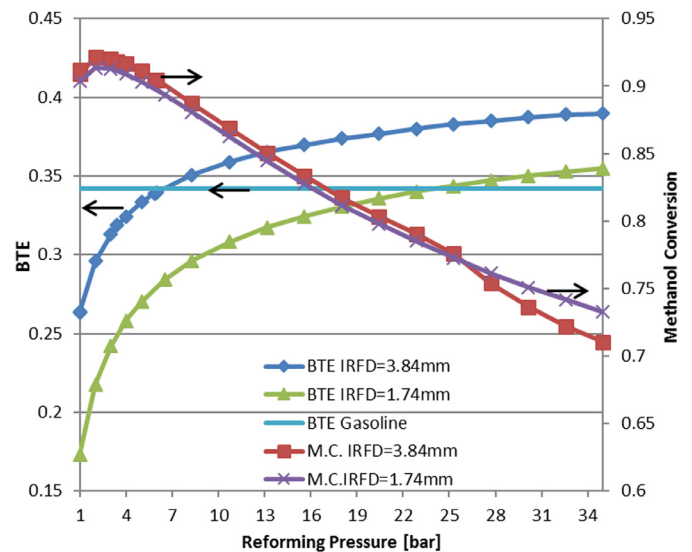
While reformate DI is the only known method that allows the use of reformate as a standalone fuel, it requires a more complex TCR system with a catalytic reformer and heat exchanger/s operating at relatively high pressures (25 – 60 bar). Availability of reformate direct injectors with a large reference flow area is essential for DI ICE with high-pressure TCR (Fig. 15) [13,131].

There are also several other noteworthy issues that might exhibit a substantial influence on the system performance, including catalyst deactivation at high pressures, the influence of reformate composition on fuel-air mixing inside the engine cylinder and subsequent combustion, and the wall-adjacent reformate flames that affect particles formation.

When different fuel reforming methods are possible and a preferred method needs to be selected together with the desirable reforming conditions, additional aspects, including catalyst stability and performance and amount of water introduced into the reforming process, should also be considered.

In summary:

- When the goal is ICE feeding with a reformate as a standalone fuel, primary fuels with low reforming temperature (e.g. methanol) should be selected. To prevent maximal power loss and abnormal combustion and to maximize efficiency and emission reduction advantages, a concept of high-pressure thermochemical recuperation with direct reformate injection to engine cylinders would be beneficial.



**Fig. 15.** Dependence of engine brake thermal efficiency (BTE) and methanol conversion (M.C.) on reforming pressure – simulation results, after Poran & Tartakovsky [13].  $P_b = 75$  kW,  $n = 4,000$  rpm, WOT,  $\lambda = 1.2$ , reformer heat transfer area =  $1.78$  m<sup>2</sup>; IRFD – injector reference flow diameter.

- When the main goal is to improve the exhaust aftertreatment performance, any primary fuel can be applied. When using conventional primary fuels (diesel fuel and gasoline), the preferred methods of fuel reforming are exhaust gas fuel reforming and plasma-assisted reforming.
- When dual-fuel operation (reformate serves as an additive in the combustion of a primary fuel) is sufficient, any primary fuel can be applied in principle. The choice of fossil fuel (gasoline, diesel fuel and natural gas) would require exhaust gas- or plasma-assisted fuel reforming as the preferred methods. Special attention should be paid to the issues of coke formation and/or catalyst sintering. The choice of an alcohol primary fuel, such as methanol and ethanol, would allow SR application. In the latter case, coke formation can be mitigated by employing an appropriate S/C ratio (Table 4).
- When a dual-fuel operation concept is applied, both direct and external (to intake manifold) methods of reformate supply to ICE are possible. Power loss and preignition will limit the amounts of reformate that can be supplied into the intake manifold.

## 9. Open questions and future research trends

While many diverse research activities have been performed in the field of onboard fuel reforming, many issues still need to be addressed to make it a viable technology. In this section we attempt to list some of these open questions:

- The issues of fuel selection and appropriate reforming technologies are summarized in Table 4 and discussed in Section 8. Given the efficient infrastructure for fuel distribution, the possibility of using gasoline for heat thermochemical recuperation should either be addressed or ruled out. Simple SR seems to be inappropriate due to the high reforming temperature required. Autothermal reforming requires modeling to determine the degree of partial oxidation required and the structure of the reformate. This should be followed by experimental verification. The use of exhaust gas reforming requires a catalyst that can withstand the expected coking.
- Amongst all the fuels reviewed herein, the main focus has been on methanol, which is already supplied in fuel stations in several countries (e.g. China). Because ethanol reforming requires higher temperatures, it has received less attention. However, ethanol has the potential of higher heat recuperation. In both cases, the effect of high pressures ( $\leq 60$  bar) and sub-stoichiometric S/C feeds should be studied.
- As emphasized herein, one of the reforming advantages is associated with the high combustion velocities of  $H_2$ . The burning velocities of various reformate compositions in conditions close to those taking place in an ICE combustion chamber should be investigated to allow further optimization of the reformate combustion process in ICE. Reformate composition can be controlled onboard, thus data on burning velocities are essential for performance optimization of engines with TCR. While the combustion velocities can be estimated from their kinetic parameters (Eq. 15), the prediction of their behavior in a mixture is more complex.
- Even though some information on penetration, mixing, and turbulent combustion of hydrogen and methane directly injected into the ICE cylinder is available, a dedicated study is required to understand the in-cylinder behavior of multicomponent reformate jets of various compositions. Unlike pure hydrogen and methane, reformate mixtures comprise constituents with very different properties (e.g.  $H_2$  and  $CO_2$ ) that can significantly alter

their behavior inside a cylinder, as compared to pure hydrogen. This knowledge is necessary for performance improvement and emissions reduction in engines fed by syngas or an onboard generated reformate.

- Further knowledge on reformates/syngas penetration, mixing, and turbulent combustion will serve as a basis for further developments in reformate direct injectors. Similar to hydrogen direct injectors [196], in reformate injectors the issue of flow rate increase is crucial.
- Compared to DI engines fed by  $H_2$ , CNG, or syngas from pressurized vessels, in DI ICEs with high-pressure TCR the issue of injection pressure should be investigated and optimized in joint consideration of engine performance and high-pressure reforming parameters.
- Research aimed at improving the startup and transient behavior of ICE with TCR is required to widen the range of possible applications. Possible solutions include (i) the use of super-capacitors and (ii) the use of partial oxidation to heat the reformer.
- Investigation of heat transfer processes in ICE with TCR is required to elucidate the optimal configuration for this complex system involving, contrary to conventional ICE, multiple processes of fuel heating, evaporation and reforming while utilizing the heat of the exhaust gas, and cooling of the reforming products before they are supplied to the engine. Further knowledge on heat transfer in ICEs with TCR is crucial for the development of compact and light automotive-scale TCR systems.
- Information on emissions of gaseous pollutants from engines fed by reformates of various compositions, including dual-fuel engine configurations, is relatively well documented. There is general agreement on the effects of the main constituents of the reformate on CO, HC, and  $NO_x$  formation. Conversely, available data on ultrafine and nanoparticle size distributions and emissions from an ICE fed by reformates is fragmentary and limited. Information on the composition and morphology of particles formed in an ICE with TCR is scarce. The low quenching distance of hydrogen, which is the main constituent of the reformate mixtures, raises questions about the possible contribution of engine lubricants to particle formation in an ICE fed by a reformate or syngas.

## 10. Summary and conclusions

Properties of hydrogen, such as wide flammability limits, low ignition energy, and very low energy density, make onboard storage and supply of hydrogen to ICE cylinders challenging. Thus, onboard production of hydrogen-rich fuels is attracting increasing interest. The possibility of syngas production from diverse sources with its subsequent use as a hydrogen-rich fuel in ICE further contributes towards the intensification of research in this field.

In principle, a wide range of energy sources can be used as primary fuels for reforming purposes. For many years, gasoline and diesel fuel have been considered as the primary fuels for onboard reforming because their usage does not require any changes in production, distribution, and fueling infrastructure. However, gasoline and diesel fuel reforming usually require temperatures  $> 1073$  K. Compared to these fossil fuels, lower alcohols, such as methanol and ethanol, exhibit some important advantages that make them suitable as primary fuels for ICE with TCR. These alcohols can be reformed at relatively low temperatures (523–573 K) using relatively cheap catalysts. Moreover, because they can be produced from both fossil and renewable feedstocks, these two alcohols are also favorable from a fuel production and availability viewpoint. Natural gas has also captured attention as a potential primary fuel. Compared to diesel fuel and gasoline, natural gas is a truly low carbon intensity fuel. The reforming temperature of methane is relatively

high 723–1023 K, therefore, similar to gasoline and diesel fuel, additional heat should be supplied to sustain endothermic reactions of methane reforming.

Many techniques have been considered for onboard fuel reforming in ICEs with TCR. Method selection depends on several factors including the primary fuel used, available heat sources, and propulsion type: (i) the simple SR approach requires relatively low reforming temperatures and was studied mainly for application to methanol and ethanol. Methanol decomposition is an advantageous process but is susceptible to catalyst deactivation. MSR may be described by the main reactions of decomposition, WGS, and possibly direct SR. When ethanol is considered as a primary fuel, the method of low-temperature ethanol reforming (based on the reaction of ethanol decomposition) can be a viable option. (ii) Partial oxidation (auto-thermal reforming) can be used when the required reforming temperature is too high, however the process is more complex. (iii) Exhaust gas fuel reforming is usually applied when gasoline and diesel are the primary fuels and applies pre-combustion (with oxygen available in exhaust gas) to alleviate the high reforming temperature required. It is considered to improve both engine and aftertreatment device performances. This process can be described by reactions of partial and complete oxidation, SR, dry reforming, WGS, methanation and others, and usually yields a mixture of products.

Information on the fundamental combustion properties of reforming products with respect to the change in the heating value of the air-fuel mixture is necessary for comprehensive analysis of the reformer-ICE system as well as for a dedicated combustion chamber design. Some progress has been made in recent years in studying the laminar burning velocity of various reformat compositions. However, data on the combustion properties of reformates at engine-relevant conditions are still lacking.

When fuel reforming is considered in an ICE with TCR, the two units are coupled. Models simulating joint operation of the reformer-ICE system have been recently developed and used in a few specific reforming applications. While the reformer model is relatively simple, various complexities can be incorporated into the ICE model and the prediction of the effect of hydrogen enrichment is challenging.

Some progress has been recently made in the design of reformers for ICEs with thermochemical recuperation. However, all these activities remain at laboratory scale. Further study, probably with more attention to monolith substrates, is required to develop reformers suitable for automotive-scale demonstrations.

Several engines utilizing various TCR concepts have been built. The experimental results prove that when a hydrogen-rich reformat is used as a standalone fuel for ICE, significant reduction in pollutant emissions together with substantial improvement in energy efficiency can be achieved. Further research is required to better understand the role of CO<sub>2</sub> in the combustion process of an ICE with TCR. The achievable emission reductions and efficiency improvements are generally proportional to the reformat hydrogen content. Evidently, the CO–CO<sub>2</sub>–CH<sub>4</sub> balance in the reforming products affects both engine performance and emissions.

New approaches have been suggested to overcome the cold start and transient behavior limitations of ICEs with TCR. Integrating the engine with TCR into a series hybrid propulsion system ensures ICE operation at a constant regime favorable for TCR, with the possibility of a reformer startup through electric heating. Further research is required to better understand the processes occurring in the ICE-TCR system during a transient event.

In-cylinder reforming avoids the need for a catalytic reformer and enables inherently good transient and startup behavior. This facilitates its implementation into engine production technologies. Despite the lower potential of in-cylinder reforming in onboard hydrogen production compared to reactor-involved fuel reforming

approaches, significant improvement in fuel economy and emissions reduction can be achieved.

It is well documented that the reformat supply to the intake manifold exhibits several limitations such as backfire, pre-ignition phenomena, and maximal power loss. In addition, accuracy of fuel flow control deteriorates when a fumigation strategy is employed. Applying the concept of direct reformat injection eliminates backfire, pre-ignition, and power loss but requires high-pressure reforming. A study on the reforming process at high-pressures together with advancements in the development of a reformat direct injector with acceptable flow rate capability are required to achieve further progress in the development of this approach.

There are still numerous subjects that require further investigation.

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