Chemical-looping combustion – a thermodynamic study

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Abstract: The poor performance of internal combustion (IC) engines can be attributed to the departure from equilibrium in the combustion process. This departure is expressed numerically, as the difference between the working fluid's temperature and an ideal 'combustion temperature', calculated using a simple expression. It is shown that for combustion of hydrocarbons to be performed reversibly in a single reaction, impractically high working fluid temperatures are required – typically at least 3500 K.

Chemical-looping combustion (CLC) is an alternative to traditional, single-stage combustion that performs the oxidation of fuels using two reactions, in separate vessels: the oxidizer and reducer. An additional species circulates between the oxidizer and reducer carrying oxygen atoms. Careful selection of this oxygen carrier can reduce the equilibrium temperature of the two redox reactions to below current metallurgical limits. Consequently, using CLC it is theoretically possible to approach a reversible IC engine without resorting to impractical temperatures. CLC also lends itself to carbon capture, as at no point is N_2 from the air allowed to mix with the CO_2 produced in the reduction process and therefore a post-combustion scrubbing plant is not required.

Two thermodynamic criteria for selecting the oxygen carrier are established: the equilibrium temperature of both redox reactions should lie below present metallurgical limits. Equally, both reactions must be sufficiently hot to ensure that their reaction velocity is high. The key parameter determining the two reaction temperatures is the change in standard state entropy for each reaction.

An analysis is conducted for an irreversible CLC system using two Rankine cycles to produce shaft work, giving an overall efficiency of 86.5 per cent. The analysis allows for irreversibilites in turbine, boiler, and condensers, but assumes reactions take place at equilibrium. However, using Rankine cycles in a CLC system is considered impractical because of the need for high-temperature, indirect heat exchange. An alternative arrangement, avoiding indirect heat exchange, is discussed briefly.

Keywords: chemical-looping combustion, oxygen carrier, carbon capture and storage, zinc, efficiency, irreversibility, lost work, Rankine cycle

1 INTRODUCTION

Haywood [**1**] argued that an internal combustion (IC) engine is a 'non-cyclic, open-circuit, steady flow, work-producing device, which can exchange heat with only one reservoir – the environment'. This definition encompasses almost all types of engine, including the obvious: gas turbines, diesel engines, and petrol engines, but also the less obvious: such as conventional power stations, which also exchange heat with only one reservoir. The efficiency of IC engines, therefore, remains of paramount importance. This paper discusses one method, which, at least theoretically, enables IC engine efficiency to be increased significantly, while retaining a heat engine as the work-producing device: chemical-looping combustion (CLC). However, before discussing CLC, the thermodynamics of a generic IC engine will be examined.

Haywood [**1**] defined the 'overall efficiency' of an IC engine as the ratio between the net work output (or external work) and the enthalpy change of the fuel's

oxidation reaction, $-\Delta H_o$, thus

$$\eta_{IC} = \frac{W_{net}}{-\Delta H_o} \tag{1}$$

Winterbone [**2**] and Haywood [**3**] showed that the maximum theoretical work output for a steady flow IC engine is equal to the fall in Gibbs function, $-\Delta G_o$, associated with the fuel's oxidation reaction.* Thus, using equation (1), the 'overall efficiency' of a reversible IC engine is given by

$$\eta_{IC,rev} = \frac{-\Delta G_o}{-\Delta H_o} = \frac{-(\Delta H_o - T_o \Delta S_o)}{-\Delta H_o} \tag{2}$$

Nature has presented the mechanical engineer with a coincidence, namely: for most hydrocarbon oxidation reactions ΔG_o is similar to ΔH_o in both magnitude and sign, hence $\Delta S_o \approx 0$ (assuming the water of combustion leaves the system as a vapour) [**4**]. Consequently, applying equation (1), the maximum efficiency of an IC engine burning a hydrocarbon is, in many instances, close to unity – alternatively

$$Q_{rej,IC,rev,HC} = (\Delta H_o - \Delta G_o)_{HC} \approx 0 \tag{3}$$

Hence, if only hydrocarbons are burnt, theoretically an 'adiabatic IC engine' can be approached. Haywood [**1**] points out engineers are unlikely to be confronted by such a machine, due to the irreversibilites inherent to complex systems of finite size. These irreversibilities lead to a requirement for additional heat transfer and, assuming this heat is rejected reversibly at T_o, the heat rejection from an irreversible IC engine is given by

$$Q_{rej,IC} = -(T_o(\Delta S_o)_{fuel} + I_{CR}) \tag{4}$$

where I_{CR} is the lost work in the control region (CR) enclosing the engine.

For hydrocarbons, equation (4) can be simplified because $\Delta S_o \approx 0$, hence

$$Q_{rej,IC,HC} \approx -I_{CR} \tag{5}$$

Therefore, the heat rejected from a hydrocarbon burning IC engine is a direct indication of the extent of irreversibility in the engine.

To illustrate the major source of irreversibility in IC engines, Fig. 1 shows a Sankey diagram for the unit boilers at Drax power station, North Yorkshire, UK, burning their design bituminous coal. The diagram shows fluxes of available energy and lost work (values used to construct this diagram were extracted from two references [**5**] and [**6**]). As Fig. 1 shows, the lost work of Drax's boilers is substantial, accounting for approximately three quarters of the lost work of the power station as a whole (the total loss of availability is ca. 63 per cent).

Kotas showed an analysis for a comparable boiler burning anthracite [**7**]. He split the boiler into three stages: adiabatic combustion, a heat transfer process from flame to the working fluid, and finally flue gas discharge. According to this analysis, the loss associated with the adiabatic combustion is approximately 65 per cent of the total boiler lost work. This equates to the combustion process destroying about 35 per cent of the fuel's available energy, resulting in the signal largest loss in a power station. Analysis of other types of IC engine yields a similar pattern, with generally high component efficiencies, but significant lost work in the combustion chamber [**8**, **9**]. Therefore, if engineers are to reduce appreciably the lost work of IC engines, then one approach is to concentrate on improving the reversibility of the combustion process.

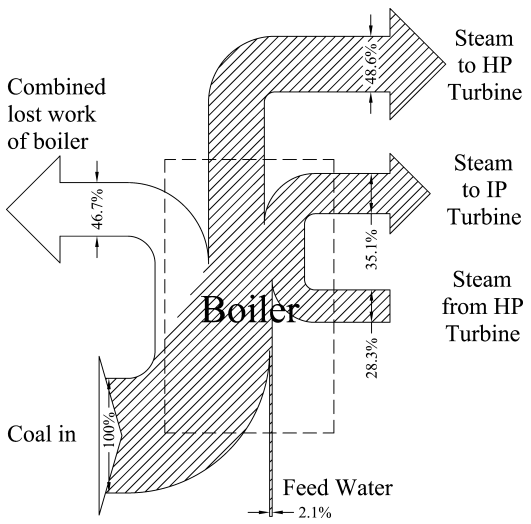

Fig. 1 Sankey diagram of availability and lost work fluxes in the boilers of Drax power station (HP – high pressure; IP – intermediate pressure)

*This assumes all streams that enter or leave the engine do so at sink conditions, T_o and P_o, and that there is a separate stream for each species. Additionally, any heat rejection from the engine must take place at T_o. These conditions ensure that no available energy flows into or out of the engine with the reactants, products, or with a heat flux, accept for the 'chemical availability' of the reactants and products.

In this work, T_o and P_o are assumed to be 298.15 K and 1 bar, respectively. As a result, thermochemical values at 'sink' condition are assumed to be identical to standard state formation values found in the literature, that is

$$\Delta G_o = \Delta G^\circ(298.15\,\text{K}, 1\text{bar})$$

$$\Delta H_o = \Delta H^\circ(298.15\,\text{K}, 1\text{bar})$$

$$\Delta S_o = \Delta S^\circ(298.15\,\text{K}, 1\text{bar})$$

The traditional approach to reducing the lost work of combustion has been to increase the average temperature at which the working fluid receives heat [**10–12**]. In a gas turbine, this can be achieved by increasing both the turbine inlet temperature (TIT) and the combustion chamber inlet temperature. Although increasing TIT is undoubtedly effective, it represents a major engineering challenge that needs little elaboration. CLC is an alternative method of increasing the reversibility of IC engines that, in principle, avoids excessively high TIT. However, before discussing CLC, the following sections examine the source of irreversibility in combustion, which leads to an approximate method of quantifying the lost work of chemical reactions in general. Using this method, a thermodynamic justification for CLC is made, before the paper concludes with a discussion of some practical aspects of CLC and an idealized analysis of a CLC system using Rankine cycles to produce shaft work.

2 IRREVERSIBILITY IN IC ENGINES AND THE REVERSIBLE REACTION TEMPERATURE

In the introduction, combustion chambers of IC engines were shown to exhibit significant irreversibility. This irreversibility is the result of a substantial departure from equilibrium that occurs in combustion reactions. For the purposes of this work, the exact nature of this departure and, hence, the actual mechanism of entropy production will not be discussed, as this is covered extensively in the literature [**13–15**]. Instead, a simple relationship for the lost work of combustion will be established.

Kjelstrup *et al.* [**16**] evaluated an 'optimal' temperature path for a chemical reaction that exhibits 'the minimum entropy production rate with constant output of product'. As part of this analysis, they showed that the lost work of a reaction can be found by integrating the Gibbs/Helmholtz relationship between the actual temperature path (they used their optimal path) and the path followed by the same reaction following an equilibrium path. Assuming that the equilibrium and actual paths are at constant temperature (this will be shown later to be a reasonable approximation), and adapting nomenclature, gives

$$I_{\mathrm{CR}} = -T_{\mathrm{o}} \left(\frac{1}{T_{\mathrm{actual}}} - \frac{1}{T_{\mathrm{eq}}} \right) \Delta H_{\mathrm{o}} \tag{6}$$

Equation (6) is identical in form to that for the lost work caused by a heat transfer across a finite temperature difference, as found in many thermodynamics texts [**17**]. Hence, the departure from equilibrium in a chemical reaction can be seen as analogous to the lost work of an irreversible heat transfer – the temperature drop equal to $(T_{\mathrm{eq}} - T_{\mathrm{actual}})$, and the heat transferred being equal to $-\Delta H_{\mathrm{o}}$.

In order to calculate the lost work of combustion using equation (6), two temperature paths are required: T_{actual} and T_{eq}. T_{actual} need not be the temperature of the reacting mixture itself; indeed, it is more useful to use the temperature of the working fluid, as equation (6) will then establish the combined lost work of both the combustion, and the loss in transferring heat from flame to working fluid. It is likely the path T_{actual} is either known, can be calculated, or can be specified in the design process. As for T_{eq}, this can be calculated using standard chemical thermodynamics that will not be described here. However, a simple relationship for T_{eq} is useful at this point. Appleby and Foulkes [**18**] derived an expression for what they described as the 'combustion temperature', T_{c}, thus

$$T_{\mathrm{c}} = \frac{\Delta H_{\mathrm{o}}}{\Delta S_{\mathrm{o}}} = T_{\mathrm{o}} \frac{\Delta H_{\mathrm{o}}}{(\Delta H_{\mathrm{o}} - \Delta G_{\mathrm{o}})} \quad (\Delta S_{\mathrm{o}} < 0) \tag{7}$$

Appleby and Foulkes argued that T_{c} represents 'the maximum temperature that can be obtained in a Carnot cycle involving the combustion of a fuel'. An alternative view is that T_{c} is the temperature at which a reaction must exchange heat with an external device such that a heat flux entering that device, equal in magnitude to $-\Delta H_{\mathrm{o}}$, can convey from the reaction all of the reactants' available energy*. This can be seen as a mechanical engineer's definition of equilibrium temperature.

The inequality $\Delta S_{\mathrm{o}} < 0$ associated with equation (7), is required because if $\Delta S_{\mathrm{o}} > 0$ then $-\Delta G_{\mathrm{o}} > -\Delta H_{\mathrm{o}}$, and the work output from the heat engine for a reversible process exceeds, in magnitude, the heat flux received by the heat engine. This would necessitate $T > \infty$ and equation (7) generates an unphysical negative temperature. However, even if $\Delta S_{\mathrm{o}} > 0$, as long as the rise in entropy is small, according to equation (4), parasitic irreversibilities in real engines will ensure that there is still a requirement to reject heat. Consequently, instances where $\Delta S_{\mathrm{o}} > 0$ have not been considered in this paper†.

*Equation (7) may also be applied to endothermic, work-consuming reactions ($\Delta H_{\mathrm{o}} > \Delta G_{\mathrm{o}} > 0$) where it predicts the minimum temperature of a heat flux capable of 'driving' the reaction to completion.

†Where $\Delta S_{\mathrm{o}} > 0$, such reactions generally exhibit an increase in the number of moles of gas from reactants to products, therefore work can be produced by direct expansion of the reacting mixture. In these cases, a balancing heat transfer from the surroundings to the IC engine is required, equal in magnitude to $T_{\mathrm{o}} \Delta S_{\mathrm{o}}$ [**18**]. This balancing heat transfer is necessary to ensure that there is a fall in the entropy of the surroundings, equal and opposite to the rise in the reacting mixture's entropy, i.e. ΔS_{o}. Consequently, there is no net entropy production – a requirement for a reversible system.

Table 1 Selected thermodynamic values for different reactions

Reaction	ΔH_o 298 K (MJ/kmol)	ΔG_o 298 K (MJ/kmol)	ΔS_o 298 K (kJ/kmol K)	T_c (K)	$\eta_{IC,rev}$ (%)
$C + O_2 = CO_2$	−393.51	−394.39	3.0	N/A	100.2
$2C_8H_{18(l)} + 25O_2 = 16CO_2 + 18H_2O_{(g)}$	−10 148.90	−10 438.44	971.1	N/A	102.9
$CH_4 + 2O_2 = CO_2 + 2H_2O_{(g)}$	−802.57	−801.11	−4.9	163 894.7	99.8
$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O_{(g)}$	−2512.50	−2452.78	−200.3	12 543.6	97.6
$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O_{(g)}$	−1323.18	−1314.40	−29.4	44 932.4	99.3
$CO + 1/2O_2 = CO_2$	−282.98	−257.23	−86.4	3276.5	90.9
$2H_2 + O_2 = 2H_2O_{(g)}$	−241.83	−228.61	−44.3	5454.0	94.5
$2H_2 + O_2 = 2H_2O_{(l)}$	−285.83	−237.14	−163.3	1750.3	83.0

Now, using the nomenclature defined above, T_{eq} in equation (6) can be replaced by the 'combustion' temperature, T_c, whereas T_{actual} is equivalent to the path followed by the working fluid, T. Using equation (7) for T_c, leads to

$$I_{CR} = T_o \left(\Delta S_o - \frac{\Delta H_o}{T} \right) \tag{8}$$

A simpler relationship was derived by El-Masri [**19**] for hydrocarbon burning engines, where $\Delta S_o \approx 0$, using similar arguments to above – he gave

$$I_{CR,HC} \approx -\frac{T_o \Delta H_o}{T} \tag{9}$$

To demonstrate the utility of equation (8) the combustion of 'design' bituminous coal in the unit boilers of Drax power station [**5**] will be considered. The combustion reaction takes the form

$$CH_{0.765}O_{0.070}N_{0.016}S_{0.013(s)} + 0.124H_2O_{(l)} + 1.17O_{2(g)} \longrightarrow CO_{2(g)} + 0.013SO_{2(g)} + 0.008N_{2(g)} + 0.507H_2O_{(g)} \tag{10}$$

Thermodynamic property values of the coal were calculated using the method of Kotas [**20**], whereas those for the other components were collated from the references [**21**] to [**24**], leading to

$$\Delta G_o = -477.7\,\text{MJ/kmol}$$

$$\Delta H_o = -483.0\,\text{MJ/kmol}$$

$$\Delta S_o = -0.0176\,\text{MJ/kmol K}$$

$$\Rightarrow T_c = T_o \frac{\Delta H_o}{\Delta H_o - \Delta G_o} = \frac{298.2 \times 483.0}{5.24} = 27\,466\,\text{K}$$

Assuming the working fluid temperature is equivalent to the maximum steam temperature for Drax of 841 K [**5**], equation (8) gives

$$I_{CR} = 298 \left(-0.0176 - \frac{(-483.0)}{841} \right) = 166.0\,\text{MJ/kmol}$$

which, as a percentage of the theoretical maximum work output (i.e. $-\Delta G_o$), gives

$$I_{\%} = \frac{166.0}{477.7} = 34.7\%$$

This value ties up well with the lost work in the real boiler of 46.7 per cent of the available energy. The actual loss is larger due to chimney losses and parasitic irreversibilites associated with any real process, such as pressure losses, heat transfer from the boiler to the surroundings, etc. However, looking at the raw figures, the loss associated with the temperature drop, $T_c - T$, is clearly larger than all the other losses put together. Hence, in order to reduce the lost work of IC engines, combustion need not be sacrificed *per se*; one can continue to use flames, but must operate with flame and hence working fluid temperature closer to T_c.

Table 1 includes thermodynamic values as well as T_c and η_{rev}, for several different reactions (collated from the references [**21**] to [**24**]). The table shows that for most hydrocarbons, ΔS_o of their oxidation reaction is small and, consequently, T_c for these reactions is invariably far higher than present day materials limits. It follows that applying equation (7), to a first approximation

$$T_{c,HC} \approx \infty \tag{11}$$

Equation (11) implies that to burn hydrocarbons efficiently in a single reaction, the necessary combustion and working fluid temperatures are impractical (and unobtainable due to dissociation) even in the most advanced gas turbines or boilers. CLC splits the hydrocarbon oxidation reaction into two redox reactions and it will be shown that, at least in principle, this enables the mechanical engineer to avoid the requirement for ultra high reaction temperatures while simultaneously enhancing reaction reversibility.

3 CHEMCIAL-LOOPING COMBUSTION

3.1 How it works

In an early paper, Richter and Knoche [**25**] described a generic system for reducing the irreversibility of combustion using thermochemical processes alone. Subsequent authors have given this system the title: chemical-looping combustion or CLC [**26**]. In CLC,

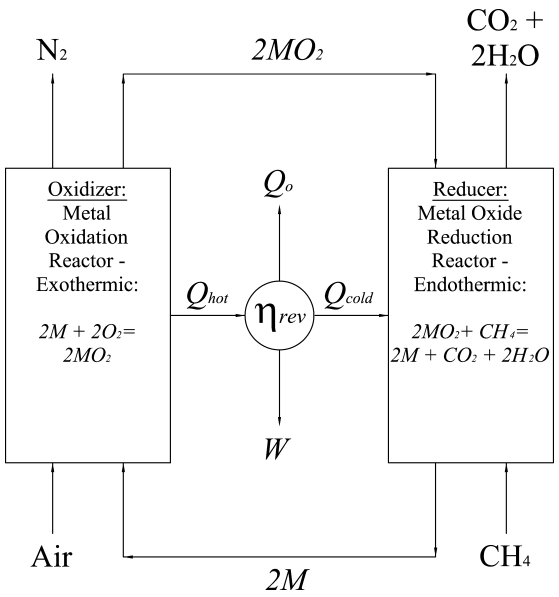

Fig. 2 Schematic diagram of ideal CLC system for power production

combustion of the primary fuel is achieved in two redox stages; two reactions are substituted for the single hydrocarbon oxidation reaction with the addition of a third species, generally called the oxygen carrier. Figure 2 shows a schematic diagram of a CLC system burning methane, using species M, as an oxygen carrier.

CLC operates in the following manner: a suitable oxygen carrier (normally a metal) is first oxidized with air in a reaction vessel (the oxidizer). This reaction is arranged to be highly exothermic and results in two easily separable products: a nitrogen-rich gaseous stream and a stream of metal oxide in a condensed state. The nitrogen-rich stream is discharged to the atmosphere, whereas the stream of metal oxide is passed to a second reaction vessel (the reducer). In the reducer, the metal oxide is converted back to metal by reaction with fuel, assumed here to be a hydrocarbon. The reduction reaction is normally endothermic and produces two easily separable streams: a stream of reduced metal in a condensed (or readily condensable) state and a flue gas consisting of CO_2, H_2O, and trace elements. The stream of metal is returned to the oxidizer for re-oxidation, thus completing the chemical loop. Meanwhile, the flue gas from the reducer can be separated into a stream of CO_2 and a stream of H_2O. The CO_2 stream can then be compressed before being transported to a storage site for sequestration. Consequently, CLC has been suggested as a viable technique for carbon capture in power stations [**26**–**30**].

To produce shaft work from CLC, the exothermic, endothermic nature of the two reactions can be exploited. Referring to Fig. 2, heat is transferred from the exothermic oxidation reaction to a heat engine, which converts a portion of the thermal availability carried with the heat flux to shaft work. The remainder of the available energy is rejected from the engine into the reducer also as a heat flux. This rejected heat, therefore, provides the 'driving force' for the endothermic reduction reaction. Depending on the value of ΔS_o, there will also be a requirement to reject a portion of heat Q_o – given by equation (4). This necessitates the addition of a second heat engine to ensure that any heat rejection takes place at T_o, and hence no available energy leaves with this heat flux. In Fig. 2, this second engine is omitted for clarity but is included in the analysis conducted later in this paper when the work output from a generic CLC system is established.

To ensure that a CLC system is reversible, the two reactions need to take place at their respective T_c's. Both these temperatures are likely to depart considerably from T_o and as a result, the reactants must be pre-heated (or pre-cooled) to their respective reaction temperatures. This can be achieved by recuperating heat from the products flowing out of the two reactors, in reversible and externally adiabatic recuperators. If the heat capacity of the product and reactant streams is assumed identical in each case, the products should leave the cycle at the same temperature as the reactants enter. This ensures that no available energy flows out of the system carried with the sensible heat of a stream. However, even when there is a significant departure from the ideal of matched heat capacities, the sensible enthalpies of reactants and products are relatively minor when compared with the enthalpies associated with chemical reactions or changes of phase, so this assumption is seen as reasonable.

3.2 Thermodynamic analysis of CLC

3.2.1 Analysis of CLC systems burning hydrocarbons ($\Delta S_o \approx 0$)

In this section, the overall efficiency of a reversible CLC system burning hydrocarbon fuels will be established. For simplicity it is assumed that $\Delta S_o \approx 0$ and hence, according to equation (3), $Q_o \approx 0$. Consequently, only a single heat engine is required, 'straddling' the two redox reactors. Starting with the definition of the overall efficiency of an IC engine, equation (1); applying this to a CLC system as a whole, gives

$$\eta_{CLC} = \frac{W_{net}}{-(\Delta H_o)_{fuel}} \tag{12}$$

W_{net} is the work output from the heat engine, thus

$$W_{net,HC} = Q_{hot}\eta_{th,engine} = -(\Delta H_o)_{oxid}\,\eta_{th,engine} \tag{13}$$

Combining equations (12) and (13), gives

$$\eta_{\mathrm{CLC,HC}} = \Psi \eta_{\mathrm{th,engine}} \tag{14}$$

where

$$\Psi = \frac{(\Delta H_\mathrm{o})_\mathrm{oxid}}{(\Delta H_\mathrm{o})_\mathrm{fuel}} \tag{15}$$

Equation (14) shows that the thermal efficiency of the heat engine is multiplied by a factor, Ψ, which depends only on the choice of fuel and oxygen carrier. In other words, for a reversible system, as Ψ increases, the temperature ratio, and hence the thermal efficiency the heat engine is required to achieve, falls as the values of T_c for each redox reaction simultaneously draw together.

The Carnot efficiency of the heat engine in a CLC system can be given a definite value if it is assumed that the engine receives and rejects heat, respectively, at the redox reactions' T_c's, as given by equation (7) – it follows

$$\eta_{\mathrm{th,Carnot,CLC,rev,HC}} = 1 - \frac{T_\mathrm{redu}}{T_\mathrm{oxid}} = 1 - \frac{(\Delta H_\mathrm{o}/\Delta S_\mathrm{o})_\mathrm{redu}}{(\Delta H_\mathrm{o}/\Delta S_\mathrm{o})_\mathrm{oxid}} \tag{16}$$

Applying Hess' law to equation (16) and simplifying gives

$$\eta_{\mathrm{th,Carnot,CLC,rev,HC}} = 1 - \left[\frac{(\Delta S_\mathrm{o})_\mathrm{oxid}}{(\Delta H_\mathrm{o})_\mathrm{oxid}}\left(\frac{(\Delta H_\mathrm{o})_\mathrm{fuel} - (\Delta H_\mathrm{o})_\mathrm{oxid}}{(\Delta S_\mathrm{o})_\mathrm{fuel} - (\Delta S_\mathrm{o})_\mathrm{oxid}}\right)\right]$$

$$\Rightarrow \eta_{\mathrm{th,Carnot,CLC,rev,HC}} = \frac{\Psi - \Omega}{\Psi\,(1 - \Omega)} \tag{17}$$

where

$$\Omega = \frac{(\Delta S_\mathrm{o})_\mathrm{oxid}}{(\Delta S_\mathrm{o})_\mathrm{fuel}} \tag{18}$$

In order to illustrate the utility of these relationships, a hypothetical reversible CLC system burning methane and using zinc as the oxygen carrier is examined. The system uses the following two redox reactions: first, the exothermic oxidation of zinc vapour

$$4\mathrm{Zn_{(g)}} + 2\mathrm{O_2} \rightarrow 4\mathrm{ZnO_{(S)}} \tag{19}$$

$$\Delta G_\mathrm{o} = -1611.7\,\mathrm{MJ/kmol}$$

$$\Delta H_\mathrm{o} = -1923.5\,\mathrm{MJ/kmol}$$

$$\Delta S_\mathrm{o} = -1.046\,\mathrm{MJ/kmol\,K}$$

$$\Rightarrow T_\mathrm{c} = T_\mathrm{oxid} = T_\mathrm{o}\frac{\Delta H_\mathrm{o}}{\Delta H_\mathrm{o} - \Delta G_\mathrm{o}} = \frac{298.2 \times 1923.5}{311.8} = 1839.4\,\mathrm{K}$$

Second, the endothermic reduction of zinc oxide, with methane*

$$\mathrm{CH_{4(g)}} + 4\mathrm{ZnO_{(s)}} \longrightarrow \mathrm{CO_{2(g)}} + 2\mathrm{H_2O_{(g)}} + 4\mathrm{Zn_{(g)}} \tag{20}$$

$$\Delta G_\mathrm{o} = +810.6\,\mathrm{MJ/kmol}$$

$$\Delta H_\mathrm{o} = +1120.9\,\mathrm{MJ/kmol}$$

$$\Delta S_\mathrm{o} = +1.041\,\mathrm{MJ/kmol\,K}$$

$$\Rightarrow T_\mathrm{c} = T_\mathrm{redu} = T_\mathrm{o}\frac{\Delta H_\mathrm{o}}{\Delta H_\mathrm{o} - \Delta G_\mathrm{o}} = \frac{298.2 \times 1120.9}{310.3} = 1077.0\,\mathrm{K}$$

Other parameters are, respectively

$$\Psi = \frac{-1923.5}{-802.6} = 2.397$$

$$\Omega = \frac{-522.8}{-4.897} = 106.8$$

$$\eta_{\mathrm{th,Carnot,CLC,rev}} = \frac{2.397 - 106.8}{2.397\,(1 - 106.8)} = 41.15\%$$

Therefore, the two redox reactions: (19) and (20), when combined, are able to oxidize methane reversibly, but with a peak system temperature, T_oxid, a manageable 1839 K instead of the high value necessary if the methane were burned in a single oxidation stage. CLC, therefore, circumvents combustion irreversibility, as the two redox reactions can both be operated close to equilibrium without excessive reaction temperatures. Critically, CLC still embodies a heat engine and hence lends itself to the application of rotating machinery.

Figure 3 represents a CLC system using the zinc-based reaction scheme and includes a Sankey diagram of the energy fluxes – units are in MJ/kmol. The diagram was drawn assuming that the heat capacities of reactants and products are matched and for brevity, the energy fluxes passing through the reversible recuperator network are not shown. As the figure shows, the oxygen carrier can also be seen as an 'enthalpy carrier'; the heat flux into the heat engine, Q_hot, is larger than the calorific value of the fuel, $-\Delta H_\mathrm{o}$, due to the circulation of a considerable portion of energy by the chemical loop.

3.2.2 *Analysis of CLC systems where* $\Delta S_\mathrm{o} < 0$

To confirm the validity of the analysis given in section 3.2.1, a thermodynamic analysis of a generic CLC system is performed, without the restriction that $\Delta S_\mathrm{o} \approx 0$. For the reasons stated in section 2, only the case where $\Delta S_\mathrm{o} < 0$ is considered. Figure 4 shows a schematic of

*The reduction of zinc oxide with methane yields carbon monoxide, largely [**31**], so this reaction scheme is used purely to illustrate the principle of enthalpy recirculation in CLC.

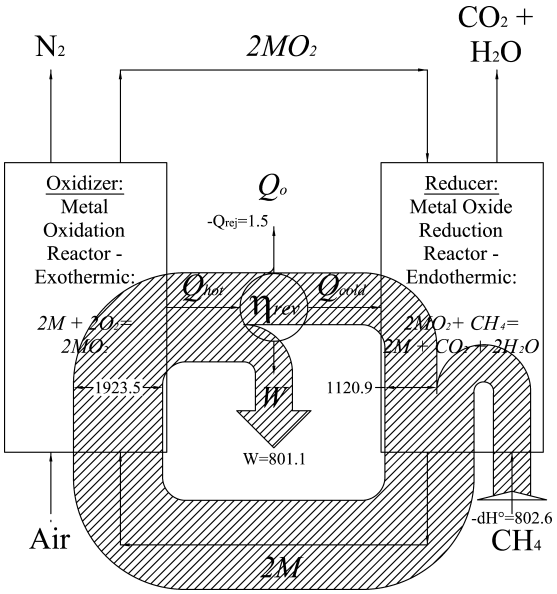

Fig. 3 Sankey diagram of energy fluxes in a reversible CLC system, where $\Delta S_o \approx 0$, and $\dot{m}Cp_{reac} = \dot{m}Cp_{prod}$

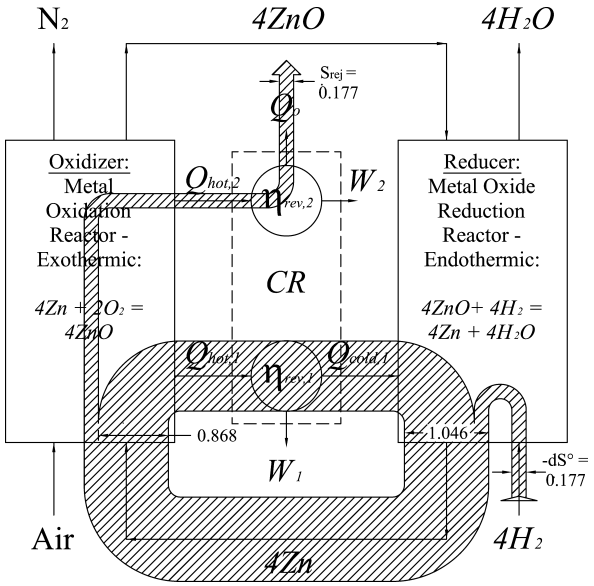

Fig. 4 Sankey diagram of reversible CLC system where $\Delta S_o < 0$, showing entropy fluxes associated with the chemical reactions and the heat rejection

a generic CLC system. Considering just the control region enclosing the heat engines as shown in Fig. 4, applying the second law leads to (from Horlock [**32**])

$$-\sum W - \sum E_Q + I_{CR} = 0 \tag{21}$$

where the work potential of a heat flux, Q, from an isothermal process at temperature, T, is given by

$$E_Q = -\left(1 - \frac{T_o}{T}\right) Q \tag{22}$$

Because $\Delta S_o < 0$, according to equation (4), for a reversible system, $Q_o = T_o \Delta S_o$ and some heat must be rejected to the environment to ensure that there is a rise in the entropy of the surroundings, equal and opposite to the fall in the reactants' entropy. To ensure that this heat rejection occurs reversibly and that no available energy is conveyed to the surroundings, a second heat engine is required, rejecting heat at T_o. Given that the system is reversible: $I_{CR} = 0$, and to calculate the work output from the system as a whole, only the non-zero work potentials that enter or leave the two heat engines need to be considered. Therefore, using equation (21) the system's net work output is given by

$$\Rightarrow -W_{net,rev} = \left(E_{Q,hot} + E_{Q,cold}\right)_{engine1} + \left(E_{Q,hot}\right)_{engine2} \tag{23}$$

To calculate the work potentials, the following is assumed: both redox reactions take place under isothermal and isobaric conditions at their respective T_c's while the heat engines deliver or receive heat, respectively, in reversible heat transfers at the respective reaction temperatures. Further, the heat capacities of the reactants and products that enter each reactor are assumed identical. If both heat engines only receive heat from the oxidation reaction, it follows

$$\left(E_{Q,hot}\right)_{engine1} = \left(1 - \frac{T_o}{(T_c)_{oxid}}\right)(\Delta H_{oxid} + Q_o) \tag{24}$$

$$\left(E_{Q,cold}\right)_{engine1} = \left(1 - \frac{T_o}{(T_c)_{redu}}\right)\Delta H_{redu} \tag{25}$$

$$\left(E_{Q,hot}\right)_{engine2} = -\left(1 - \frac{T_o}{(T_c)_{oxid}}\right) Q_o \tag{26}$$

Substituting these work potentials into equation (21) and using equation (7) for the two T_c's gives

$$\begin{aligned} -W_{net,rev} = &\left(1 - T_o\left(\frac{\Delta S_o}{\Delta H_o}\right)_{oxid}\right)(\Delta H_{oxid} + Q_o) \\ &+ \left(1 - T_o\left(\frac{\Delta S_o}{\Delta H_o}\right)_{redu}\right)\Delta H_{redu} \\ &- \left(1 - T_o\left(\frac{\Delta S_o}{\Delta H_o}\right)_{oxid}\right) Q_o \end{aligned} \tag{27}$$

Simplifying and eliminating terms leads to

$$-W_{net,rev} = (\Delta H_o - T_o \Delta S_o)_{oxid} + (\Delta H_o - T_o \Delta S_o)_{redu} \tag{28}$$

$$\Rightarrow -W_{net,rev} = (\Delta G_o)_{oxid} + (\Delta G_o)_{redu} \tag{29}$$

Applying Hess' Law for a reversible process, the values of ΔG_o for the two reactions must sum to that of the

primary hydrocarbon oxidation process, thus

$$(\Delta G_o)_{oxid} + (\Delta G_o)_{redu} = (\Delta G_o)_{fuel} \quad (30)$$

Combining equations (29) and (30) gives

$$W_{net,rev} = -(\Delta G_o)_{fuel} \quad (31)$$

As expected, a reversible CLC system achieves the same theoretical maximum work output as a conventional IC engine, but critically, high process temperatures can be avoided. To facilitate a better understanding of why this is the case, a CLC system burning hydrogen, forming water vapour, will be analysed. The reaction has the following thermodynamic values

$$4H_{2(g)} + 2O_{2(g)} \longrightarrow 4H_2O_{(g)} \quad (32)$$

$$\Delta G_o = -914.4\,\text{MJ/kmol}$$

$$\Delta H_o = -967.3\,\text{MJ/kmol}$$

$$\Delta S_o = -0.177\,\text{MJ/kmol K}$$

$$\Rightarrow T_c = T_{redu} = T_o \frac{\Delta H_o}{\Delta H_o - \Delta G_o} = \frac{298.2 \times 967.3}{52.86} = 5456\,\text{K}$$

A chemical loop able to perform the overall reaction (32) consists of the oxidation of zinc, reaction (19), followed by the reduction of zinc oxide with hydrogen

$$4H_{2(g)} + 4ZnO_{(s)} \longrightarrow 4H_2O_{(g)} + 4Zn_{(g)} \quad (33)$$

$$\Delta G_o = +697.2\,\text{MJ/kmol}$$

$$\Delta H_o = +956.1\,\text{MJ/kmol}$$

$$\Delta S_o = +0.868\,\text{MJ/kmol K}$$

$$\Rightarrow T_c = T_{redu} = T_o \frac{\Delta H_o}{\Delta H_o - \Delta G_o} = \frac{298.2 \times 956.1}{258.9} = 1101.1\,\text{K}$$

Figure 4 shows the fluxes of entropy in this reversible system – units are MJ/kmol K. The diagram illustrates a key feature of CLC, that is, it enables entropy to be recirculated. This means that even if $\Delta S_o \approx 0$ for the primary fuel oxidation reaction, both the oxidation and reduction stages can nonetheless exhibit a sizeable but equal and opposite change in entropy. This is why both reactions can take place reversibly and, according to equation (7), at reasonable temperatures.

The original justification for adopting CLC was the improvement in overall efficiency due to the enhanced reaction reversibility [**25**, **28**]. However, despite its theoretical benefits, to implement CLC in practice requires a significant increase in plant complexity and cost, and it is likely that CLC would have been forgotten, but for the current interest in carbon capture technologies.

3.3 CLC and carbon capture

Carbon capture has revived interest in CLC primarily because the technology has a distinct advantage over many other carbon capture techniques, in that at no point is a 'difficult' gas separation process required. 'Difficult', in this context, means the removal of a practically non-condensable gas, CO_2, at low partial pressure from a mixture of other non-condensable gases, principally nitrogen. To perform this operation, chemical or physical scrubbing is normally required. McGlashan and Marquis [**33**] have shown that the minimum, theoretical work input required to remove CO_2 from flue gas is not significant – typically about 3 per cent of the primary energy input in to a power station. However, they went on to show that practical scrubbing systems have a second law efficiency in the region of 30 per cent, which explains the considerable work input required in carbon capture plant. CLC avoids altogether the need to separate gases at low partial pressure, by never mixing the gases in the first place. The only separation process required is the removal of H_2O from the CO_2 stream, and much of this H_2O will separate in the intercoolers of the CO_2 compression system (assuming the CO_2 is being sequestrated). If further drying of the CO_2 is necessary, a post-compression dehydration could be specified using standard techniques common to the gas industry [**34**].

4 SELECTING AN OXYGEN CARRIER

4.1 Thermodynamic criteria

So far, CLC has been considered only as a theoretical concept. Some of the practical aspects of CLC will now be examined by considering the selection criteria for the oxygen carrier, and specifically thermodynamic selection criteria.

The oxygen carrying species must fulfil a number of thermodynamic requirements. To reduce the irreversibility of an IC engine, CLC introduces a surrogate species that allows, within limits, the entropy change of the two redox reactions to be selected. Consequently, according to equation (7), this enables the value of T_c for each reaction to be reduced to a value below a limiting TIT. However, the ΔS_o of the two redox reactions are constrained to sum to the value of ΔS_o for the basic hydrocarbon oxidation process as follows

$$(\Delta S_o)_{oxid} + (\Delta S_o)_{redu} = (\Delta S_o)_{HC} \approx 0 \quad (34)$$

Hence, in CLC systems burning hydrocarbons, to satisfy equation (34), it is necessary to find two reactions that have, respectively, a fall and a rise in ΔS_o. In addition, according to equation (7), the value of the entropy change for each reaction needs to be significant to ensure that the reaction temperatures are below current metallurgical limits. How can this be achieved in practice?

Starting first with the oxidation process, assuming that the reaction is both exothermic and spontaneous (i.e. work-producing), because ΔH_o is negative in sign, and studying equation (7), to produce a positive T_{oxid}, ΔS_o for this reaction must be negative (as it is for many, but not all work-producing reactions). A drop in ΔS_o takes place if there is a reduction in the number of gaseous moles of products relative to reactants. The easiest way of achieving this is to perform a reaction between gaseous reactants that results in the formation of a product, or products, in a condensed state. Good examples of reactions of this type are the combustion of metals in the gaseous state forming refractory, or at least involatile, oxides. Equation (19) is one such example.

As for the reduction process, assuming that this is both endothermic and non-spontaneous (i.e. work-consuming), if equation (7) is applied again, for a positive T_{redu}, ΔS_o must also be positive. This can be achieved by ensuring that some or all of the reactants are in a condensed state, with the reaction producing gaseous products. Examples of reactions of this type are the reduction of condensed metal oxides with solid fuels producing products partly or completely in the gaseous state. However, the reaction of metal oxides with gaseous reducing agents is likely to be faster and there can still be a considerable rise in ΔS_o in reactions of this type. Equation (20) is one such example.

Satisfying equation (34), and hence achieving a fall and rise, respectively, in ΔS_o for the two redox reactions, is not a sufficient criteria for selecting an oxygen carrier. It is also essential to aim for a suitable pairing of reaction temperatures. The oxidation process needs to be the hotter of the two processes to ensure that it can supply heat, via the heat engine, to the cooler reduction process. Ideally, the oxidation reaction would be as hot as present day metallurgical constraints will allow, so that its reaction velocity is as high as possible. Equally, although the temperature of the reduction reaction must be lower than that of the oxidation process, it must still be sufficiently high to ensure that its rate of reaction is not too sluggish.

From equation (34), one can obtain some information about the possible temperatures of the two reactions. Rearranging equation (7), a relationship for the ΔS_o in terms of the ΔH_o and the T_c is obtained

$$\Delta S_o = \frac{\Delta H_o}{T_c} \tag{35}$$

Substituting equation (35) into equation (34), for hydrocarbon combustion it follows

$$\left(\frac{\Delta H_o}{T_c}\right)_{oxid,HC} + \left(\frac{\Delta H_o}{T_c}\right)_{redu,HC} \approx 0 \tag{36}$$

$$\Rightarrow -\left(\frac{(\Delta H_o)_{oxid}}{(\Delta H_o)_{redu}}\right) \approx \left(\frac{T_{oxid}}{T_{redu}}\right)_{HC} \tag{37}$$

Applying Hess' law, and substituting equation (15) into equation (37) leads to

$$\left(\frac{\Psi}{\Psi - 1}\right) \approx \left(\frac{T_{oxid}}{T_{redu}}\right)_{HC} \tag{38}$$

Now, if T_{oxid} is constrained to be less than a maximum TIT, for a fast reaction, T_{redu} must be as high as possible, which clearly means that the values of ΔH_o for both reactions should be similar, alternatively Ψ should be as high as possible. The problem with this approach is that, as the two reaction temperatures draw together, the efficiency of the heat engine in Fig. 3 falls, so the circulation of energy in the chemical loop must increase if a high overall efficiency is to be maintained. This increased circulation can be achieved by using strongly energetic reactions; alternatively, a large inventory of circulating oxygen carrier will be required. Both of these approaches are undesirable due to a likely increase in the lost work caused by parasitic losses.

4.2 Other selection criteria

If the reaction temperatures of both redox reactions are high, the temperature stability of an oxygen carrier becomes important. Biology uses chemical looping to affect respiration and is able to use complex organic and metal-organic chemicals as oxygen carriers (haemoglobin, etc.), but such complex chemicals lack sufficient temperature stability for application to industrial power generation. Indeed, the search for an oxygen carrier becomes more manageable if only elements or simple mixtures of the elements are considered. The search can be further constrained to elements that are low in price and, along with their oxides, satisfy the criteria of being non-toxic.

Table 2 shows, for a range of elemental oxygen carriers, values of Ψ and Ω, the elements' boiling point, T_c for both the resulting redox reactions, and the η_{th} of the Carnot engine straddled between the two redox reactions. The fuel is assumed to be carbon, although different hydrocarbons give similar values. The table is arranged in the ascending order of reversible oxidation temperature, T_{oxid}. Thermodynamic constants used to construct Table 2 were collated from the references [**21**] to [**24**].

As can be seen from Table 2, there is a general trend that the more volatile elements exhibit a lower T_{oxid},

Table 2 Useful values for the selection of an oxygen carrier (fuel = carbon)

Element	T_{Bpt} (K)	Oxidation reaction	T_{oxid} (K)	Reduction reaction	T_{redu} (K)	Ψ	Ω	$\eta_{th,Carnot,CLC}$ (%)
Potassium	1032	$4K_{(g)}+O_2 \rightarrow 2K_2O_{(s)}$	1715.6	$C_{(s)} + 2K_2O_{(s)} \rightarrow CO_{2(g)} + 4K_{(g)}$	1087.0	2.751	−213.8	36.64
Cadmium	1038	$2Cd_{(g)}+O_2 \rightarrow 2CdO_{(s)}$	1795.9	$C_{(s)}+2CdO_{(s)} \rightarrow CO_{2(g)}+2Cd_{(g)}$	835.3	1.881	−139.7	53.49
Zinc	1180	$2Zn_{(g)} + O_2 \rightarrow 2ZnO_{(s)}$	1839.4	$C_{(s)}+2ZnO_{(s)} \rightarrow CO_{2(g)}+2Zn_{(g)}$	1080.7	2.444	−177.1	41.25
Sodium	1154	$4Na_{(g)}+O_2 \rightarrow 2Na_2O_{(s)}$	1845.5	$C_{(s)}+2Na_2O_{(s)} \rightarrow CO_{2(g)} + 4Na_{(g)}$	1221.7	2.986	−215.7	33.80
Lead	2022	$2Pb_{(l)} + O_2 \rightarrow 2PbO_{(s)}$	2054.9	$C_{(s)} + 2PbO_{(s)} \rightarrow CO_{2(g)}+2Pb_{(l)}$	244.8	1.137	−73.79	88.09
Nickel	3157	$2Ni_{(s)}+O_2 \rightarrow 2NiO_{(s)}$	2482.2	$C_{(s)} + 2NiO_{(s)} \rightarrow CO_{2(g)}+2Ni_{(s)}$	445.5	1.223	−65.68	82.05
Tin	2875	$Sn_{(l)} + O_2 \rightarrow SnO_{2(s)}$	2642.0	$C_{(s)} + SnO_{2(s)} \rightarrow CO_{2(g)}+Sn_{(l)}$	852.4	1.486	−74.98	67.74
Cobalt	3200	$2Co_{(s)}+O_2 \rightarrow 2CoO_{(s)}$	2914.0	$C_{(s)} + 2CoO_{(s)} \rightarrow CO_{2(g)} + Co_{(s)}$	505.7	1.208	−20.35	83.58
Iron	3134	$\frac{4}{3}Fe_{(s)} + O_2 \rightarrow \frac{2}{3}Fe_2O_{3(s)}$	2960.7	$C_{(s)} + 2Fe_2O_{3(s)} \rightarrow CO_{2(g)} + \frac{4}{3}Fe_{(s)}$	827.2	0.931	−41.92	N/A
Tungsten	6173	$\frac{2}{3}W_{(s)} + O_2 \rightarrow \frac{2}{3}WO_{3(s)}$	3189.2	$C_{(s)} + \frac{2}{3}WO_{3(s)} \rightarrow CO_{2(g)} + \frac{2}{3}W_{(s)}$	940.1	1.428	−59.70	70.52
Calcium	1757	$2Ca_{(g)} + O_2 \rightarrow 2CaO_{(l)}$	3767.4	$C_{(s)} + 2CaO_{(l)} \rightarrow CO_{2(g)} + 2Ca_{(g)}$	2738.4	3.736	−132.2	27.31

i.e. their oxides are less stable. This is despite the fact that many of the volatile elements shown exhibit a strong affinity for oxygen [**35**]. This apparent paradox can be explained by considering the change in the number of gaseous moles when a volatile element burns forming an involatile oxide, which leads to a correspondingly large ΔS_o. As a result, even though the oxidation process is highly energetic, the value of T_c given by equation (7) is still quite low. Volsky and Sergievskaya discuss this subject further [**35**].

Considering the applicability of specific elements to an actual CLC system, one option is to use alkali metals. Both sodium and potassium are cheap and of low toxicity. In addition, both metals occur in the ash of many coals [**36**], so there is the prospect that a power station could be 'self-sufficient' in oxygen carrier. A weakness of the alkali metals is the volatility of their oxides and, as a result, chimney emissions of alkali metal compounds may be a problem.

Of the non-alkali metals, cadmium exhibits the lowest oxidation temperature, but its reduction temperature is a little cool*. Cadmium is also expensive and highly toxic, and has been ruled out for these reasons. Zinc, a close homologue of cadmium, has a T_{oxid} only slightly higher than cadmium, but its reduction temperature is significantly higher. Zinc is also cheap and relatively non-toxic. Of the other elements, none have an oxidation temperature close to present day metallurgical limits and so will not be discussed further.

5 WORK OUTPUT FROM CLC SYSTEMS

5.1 Work output and efficiency of irreversible CLC systems

How can work be extracted from the two redox reactions in a real-life CLC power station? Referring to Fig. 2, one needs to construct a thermodynamic cycle which 'straddles' the two reaction vessels – receiving heat from the oxidizer and rejecting heat into the reducer. Equation (14) can be used to calculate the overall efficiency of such a system, but this relationship is only correct if the process is reversible and if the fuel's $\Delta S_o \approx 0$. If either of these requirements is unsatisfied, heat exchange with the surroundings becomes necessary. If the available energy contained within this heat flux is to be converted to shaft work, a second heat engine is then required, ultimately rejecting heat to the surroundings at T_o. Therefore, to establish a more general relationship for the efficiency of a CLC system, the combined work output of both the primary and secondary heat engines must be considered, and hence, equation (12) becomes

$$\eta_{CLC} = \frac{W_{net,engine1} + W_{net,engine2}}{-(\Delta H_o)_{fuel}} \tag{39}$$

The work output from the primary heat engine is given by the simple relationship

$$W_{net,engine1} = -(\Delta H_o)_{oxid}\, \eta_{th,engine1} \tag{40}$$

Assuming again that the CLC system is burning a hydrocarbon, if the heat engine is reversible, its heat rejection would be numerically equal to the ΔH_o of the endothermic reduction process, and no additional heat rejection would be required. With an irreversible heat engine, more heat is rejected by the engine than required to 'drive' the reduction reaction. This extra Q_{rej} is numerically equal to the difference between the work outputs of a reversible engine and the actual heat engine, thus

$$Q_{rej,HC} = (\Delta H_o)_{oxid}\left[\eta_{th,Carnot} - \eta_{th,engine1}\right] \tag{41}$$

Therefore, an additional quantity of heat, given by equation (41), must be withdrawn from the primary heat engine at its T_{cold} (i.e. T_{cond} if a Rankine cycle is

*Cadmium was the oxygen carrier chosen by the originators of chemical-looping combustion – Richter and Knoche [**25**].

used). This parcel of heat can be used in a second heat engine, the work output of which is given by

$$W_{\text{net,engine2,HC}} = -(\Delta H_{\text{o}})_{\text{oxid}} \left[\eta_{\text{th,Carnot}} - \eta_{\text{th,engine1}}\right] \eta_{\text{th,engine2}} \quad (42)$$

Substitution of equations (40) and (42) in to equation (39) leads to a relationship for the overall efficiency of a CLC system burning hydrocarbons, but allowing for heat engine irreversibilities

$$\eta_{\text{CLC,HC}} = \Psi \left[\begin{array}{l} \eta_{\text{th,engine1}} \left(1 - \eta_{\text{th,engine2}}\right) \\ +\eta_{\text{th,Carnot}} \eta_{\text{th,engine2}} \end{array} \right] \quad (43)$$

5.2 CLC-Rankine systems

The analysis in the previous section did not consider the type of heat engine applicable to both the primary and secondary heat engines. What engines are suitable? One possible way to implement a CLC system is to use Rankine cycles. Figure 5 shows a schematic of a CLC system embodying a single Rankine cycle (the second heat engine has been omitted for sake of brevity, but will be considered in the analysis given later). The arrangement uses indirect heat transfer to exchange heat between the oxidation and reduction reactions, using a boiling and condensing working fluid, respectively. The recuperators necessary to recover heat from exiting flue gas to the incoming reactants have been omitted for clarity. To ensure the process is as efficient as possible, T_{hot} and T_{cold} of the Rankine cycle should be close to the T_{c}'s of the two redox reactions. This means, of course, that the temperatures involved are extremely high, which rules out

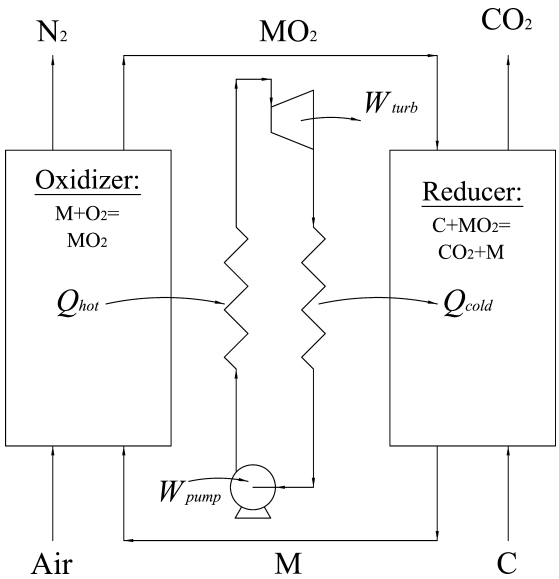

Fig. 5 Schematic diagram of a simple CLC system using a Rankine cycle for power generation

steam as a working fluid – what are the alternatives to steam for this application?

El-Wakil [**37**] and Angelino and Invernizzi [**38**] discussed the application of high temperature Rankine cycles to nuclear and coal-fired power stations, respectively. Plotkowiak [**39**] studied Rankine cycles in space power applications, examining both cycle thermodynamics and the suitability of different working fluids. All these authors concluded that metal vapours are the most suitable working fluid at high temperature because of their thermal stability and favourable thermodynamic properties. Space power Rankine cycles, however, are of particular interest as they are characterized by a high condenser temperature. This is because, in space, heat can only be rejected using radiation heat transfer from a high temperature radiant panel heated directly by the (condensing) working fluid [**40**]. In a CLC system, heat must also be rejected at high temperature as the T_{c} of the reduction reaction determines this temperature. Consequently, in both CLC and space power, excessively low condenser pressure can be avoided.

A further advantage of metal vapour Rankine cycles is the reducing conditions that prevail in high temperature parts of these engines. In conventional Rankine cycle practice, the strongly oxidizing conditions in both boilers and turbines restrict materials choice, predominantly, to the extended-stainless steel family. This is unfortunate because the relatively low melting point of these alloys limits their creep resistance. However, if reducing or neutral conditions prevail, the refractory metals can be considered as constructional materials, as then their poor oxidation resistance is not a restriction – refractory metals have substantially higher creep strength than the extended-stainless steels [**41**].

Bevard and Yoder [**42**] review recent work on metal vapour Rankine cycles applied to space power systems, many of which used refractory metals extensively for both boiler and turbomachinery components. The review details the operating experience with alkali metal boilers and turbines running at temperatures up to 1100 K and with reasonable life times (thousands of hours). However, it is also argued that metal vapour Rankine cycles with working fluid temperatures of 1500 K or even higher may be possible with further materials developments.

5.3 An irreversible CLC system

A 'practical' CLC system burning coal, using Rankine cycles for the two heat engines and using zinc as the oxygen carrier will now be analysed. Sodium has been chosen as the working fluid for the primary Rankine cycle, whereas water substance has been selected for the second Rankine cycle. The second Rankine cycle

Table 3 Thermodynamic conditions for Rankine cycles of irreversible CLC system

	T (K)	P (kPa)	H (MJ/kmol)	S (MJ/kmol K)
Rankine cycle 1				
Saturated Na vapour at $T_{\text{boil},1}$	1819.4	4461.5	120.90	0.1525
Saturated Na vapour at $T_{\text{cond},1}$	1100.7	58.37	116.76	0.1794
Turbine exit isentropic	1100.7	58.37	87.18	0.1525
Turbine exit $\eta_{\text{isen}} = 90$ per cent	1100.7	58.37	90.55	0.1556
Saturated Na liquid at $T_{\text{cond},1}$	1100.7	58.37	26.36	0.0973
Rankine cycle 2				
Superheated steam at $T_{\text{boil},2}$	823.2	10 000	63.05	0.1217
Saturated steam at $T_{\text{cond},2}$	309.2	5.9	46.25	0.1502
Turbine exit isentropic	309.2	5.9	37.45	0.1217
Turbine exit $\eta_{\text{isen}} = 85$ per cent	309.2	5.9	41.29	0.1341
Saturated water at $T_{\text{cond},2}$	309.2	5.9	2.71	0.0093

uses as its source of heat, condensing sodium from the primary Rankine cycle at a temperature of

$$T_{\text{boil},2} = T_{\text{redu}} - \Delta T_{\text{appr}} = 1080.7 - 20 = 1060.7 \text{ K}$$

where ΔT_{appr} is the approach temperature between condensing sodium and boiling water.

A TIT of 1060.7 K is high for steam plant, so a more appropriate $T_{\text{boil},2}$ of 823.2 K has been selected, being typical of subcritical steam plant practice. The difference between this temperature and that of the condensing sodium means there would be substantial entropy production in the secondary Rankine cycle boiler. However, the second Rankine cycle is required to produce relatively little power so this loss is considered acceptable.

Further assumptions used in the analysis are listed below:

1. Coal is considered to be graphite and ashless.
2. Both redox reactions operate at their respective T_c's.
3. Pressure losses are negligible.
4. Sodium Rankine cycle:
   (a) sodium vapour leaves the boiler with no superheat;
   (b) liquid sodium leaves the condenser as saturated liquid;
   (c) sodium boiler feed pump work is zero;
   (d) turbine isentropic efficiency, η_{isen}, of 90 per cent;
   (e) all boilers and condensers operate with an approach temperature, $\Delta T_{\text{appr}} = 20$ K.
5. Steam Rankine cycle:
   (a) minimum cycle temperature 309.2 K;
   (b) maximum working pressure assumed to be 10 MPa, with steam superheated at boiler exit;
   (c) liquid water leaves the condenser as saturated liquid – i.e. no feed heating;
   (d) water boiler feed pump work is zero;
   (e) turbine isentropic efficiency, η_{isen}, of 85 per cent.

Making these assumptions, the cycle conditions for the two Rankine cycles are given in Table 3 (sodium's thermodynamic properties were calculated using data from the references [**43**] to [**45**], whereas properties for water substance were extracted from Haywood [**46**]).

To calculate the efficiency of the Rankine cycles with zero feed pump work, the following formula from Haywood [**47**] can be used

$$\eta_{\text{Rankine}} = \frac{h_{\text{hot}} - h_{\text{cold,turb}}}{h_{\text{hot}} - h_{\text{cold,cond}}} \tag{44}$$

Substituting conditions from Table 3 into equation (44), gives

$$\eta_{\text{engine},1} = \frac{120.90 - 90.55}{120.90 - 26.36} = 32.1\%$$

and

$$\eta_{\text{engine},2} = \frac{63.05 - 41.29}{63.05 - 2.71} = 36.1\%$$

Therefore, substituting these two efficiency values into equation (43), along with the appropriate values of Ψ, Ω, and η_{Carnot} from Table 2, gives

$$\eta_{\text{CLC}} = 2.444\,[0.321\,(1 - 0.361) + 0.361 \times 0.413]$$
$$\Rightarrow \eta_{\text{CLC}} = 86.5\%$$

Optimization and the addition of the normal reheating and regeneration methods, common to standard Rankine cycles, would lead to further improvements in this overall efficiency. Nonetheless, it is worth comparing this efficiency value with that possible from a simple heat engine using the same peak and sink temperatures, thus

$$\eta_{\text{Carnot}} = 1 - \frac{298.2}{1839.4} = 83.8\%$$

These results confirm that the efficiency of a CLC system is not limited to the Carnot efficiency for the

same peak temperature and sink condition. However, the practical difficulties of constructing and operating such a pair of Rankine cycles appear insurmountable. In particular, the maximum working fluid temperature (1819 K) is far higher than current boiler technology can withstand (even using refractory metal tubing). To circumvent this design problem, ideally, the use of indirect heat exchange to generate a hot working fluid should be avoided, as then there would be no need to expose a tube wall to both high temperatures and a high pressure differential. In a gas turbine, the working fluid and the combusting mixture are one in the same; this enables gas turbines to operate with TIT well above those of conventional Rankine cycles; indirect heat exchange at peak temperature is not required. The combination of a gas turbine with a CLC cycle is discussed briefly in the following section.

5.4 The CLC-gas turbine

To avoid indirect heat exchange in a CLC system, the products from the oxidation reaction could be passed straight though a turbine as in conventional gas turbine practice. The exhaust from this turbine could then be passed directly to the reducer – the enthalpy of the exhaust gases providing the necessary availability to drive the endothermic reduction reactions. However, there is a problem with this arrangement, as was argued earlier, the advantage that CLC has over competing carbon capture technologies is that nitrogen from the air used in combustion is not mixed with CO_2. Clearly, if the combustion chamber exit gas ends up in the reducer, so will all the nitrogen, mixing with the CO_2. Ideally, an alternative method of generating a hot working fluid without an interceding wall is required, which can transfer heat from a reacting mixture inundated with nitrogen to a working fluid, while avoiding contamination of the working fluid by the nitrogen.

Use of radiation heat transfer, instead of indirect heating of the working fluid, may be a solution to this problem. Brzustowski and Glassman [**48**] argued that metal combustion zones exhibit a high emissivity due to the concentration of condensed species (principally oxides) – something that has been exploited historically in flash bulbs [**49**]. Now, if the various species in the oxidizer can be stratified, it may be possible to form a region of vapour, free of nitrogen, adjacent to a burning mixture – a region of metal vapour, for instance. If the vapour in this region is sufficiently opaque or contains suspended matter, radiation from the combustion could be used to heat this vapour before it is drawn off. Thus, hot, nitrogen-free working fluid would be produced ready for subsequent expansion. The feasibility of this technique is being explored currently.

6 CONCLUSIONS

The irreversibility of hydrocarbon combustion and the consequent poor performance of IC engines relates to the departure from equilibrium in the combustion chamber. This departure can be seen as analogous to the temperature drop between an ideal and the actual combustion event. Consequently, to achieve high efficiency, IC engines must operate at an impractically high cycle temperature when using single-stage combustion. Using CLC the single, irreversible combustion event is replaced with two redox reactions: an exothermic oxidation reaction where a metallic oxygen carrier is 'burned' forming a metal oxide; and an endothermic reduction reaction where the metal oxide is reduced back to the metal by a fuel. Both the redox reactions can be conducted reversibly at temperatures below present materials limits given an appropriate choice of oxygen carrier. Therefore, using CLC, an engine can, in principle, be constructed which is able to produce the maximum theoretical work output, without requiring excessive cycle temperatures.

The efficiency of a CLC system burning a hydrocarbon is given by the product of two quantities: the thermal efficiency of a heat engine receiving heat from the oxidation reactor and rejecting heat into the reduction reactor; and a factor, Ψ, equivalent to the ratio of the ΔH_o of the oxygen carrier's and fuel's oxidation reaction, respectively. This factor is greater than unity when common metals are used as the oxygen carrier – the choice of fuel is relatively unimportant as long as it is a hydrocarbon.

A 'practical' CLC system can be constructed using two Rankine cycles to generate shaft work. Even allowing for the irreversibility associated with turbine expansion and temperature drops in the condenser and boiler, the resulting overall efficiency is still high when compared with other systems operating with the same peak temperature. Despite the high theoretical efficiency, using high temperature Rankine cycles in CLC systems is impractical, and an alternative CLC-gas turbine arrangement is proposed for future studies.

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APPENDIX

Notation

EQ	work potential of a heat flux (MJ/kmol)
G	Gibbs function (MJ/kmol)
H	enthalpy (total) (MJ/kmol)
I	irreversibility or lost work (MJ/kmol)
P	pressure (bar)
Q	heat flux (MJ/kmol)
R	universal gas constant = 8.3144 (MJ/kmol K)
S	entropy (absolute) (MJ/kmol K)
T	thermodynamic temperature (K)
W	shaft work (MJ/kmol)
Δ	change in property due to a chemical reaction – products minus reactants
η	efficiency
Ψ	ratio of enthalpy of oxidation reactions
Ω	ratio of entropy of oxidation reactions

Subscripts/superscripts

appr	approach temperature
c	'combustion' temperature
Carnot	Carnot engine
cold	cold stream or heat flux
cond	condenser
CR	control region
engine	(heat) engine
fuel	fuel
(g)	gaseous state
hot	hot stream or heat flux
HC	hydrocarbon
IC	internal combustion engine
in	stream flowing into a process
isen	isentropic process
(l)	liquid state
net	net work
o	standard state or sink condition (25 °C, 1 bar)
out	stream flowing out of a process
oxid	oxidation reaction
prod	products
pump	feed pump
Q	relating to a heat flux
Rankine	Rankine cycle
reac	reactants
redu	reduction reaction
rej	heat rejection
rev	reversible process
(s)	solid state
th	thermal (efficiency)
turb	turbine