Chemical looping combustion of coal

Colin Henderson

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Abstract

Chemical looping combustion is an indirect form of combustion in which an oxygen-containing solid material, typically a metal oxide, supplies the oxygen to a fuel, and the spent oxygen ‘carrier’ is separately regenerated by high temperature reaction in an air stream. As there is no direct contact between air and fuel, CO_2 recovery up to very high levels is simplified. There is also potential for higher efficiency in delivery of energy than for conventional combustion or gasification with CO_2 capture. More elaborate chemical looping systems are also a future possibility for hydrogen production. This report describes the ongoing laboratory work to develop and test oxygen carriers and describes the continuous process development units that are being used to establish the proof-of-concept. Power cycles that could use chemical looping are also described. The focus of the report is on coal and coal-derived syngas, but some work with natural gas is included. The technology on coal has reached the scale of 1 MWth in the form of a continuous plant in Germany, recently commissioned.

Acronyms and abbreviations

CC	combined cycle
CDCL	coal direct chemical looping
CFBC	circulating fluidised bed combustion
CLC	chemical looping combustion
CLOU	chemical looping with oxygen uncoupling
DSC	differential scanning calorimetry
ECSC	European Coal and Steel Community
EU	European Union
FTIR	Fourier transform infrared spectroscopy
ID	internal diameter
IEA	International Energy Agency
IGCC	integrated gasification combined cycle
kWth	kilowatts, thermal
LHV	lower heating value
MPa	megapascals
MS	mass spectrometer (or mass spectrometry)
MWth	megawatts, thermal
NETL	National Energy Technology Laboratory (US DOE)
NGCC	natural gas combined cycle
NOx	oxides of nitrogen (NO and NO_2)
PCC	pulverised coal combustion
PDU	process development unit
ppm(v)	parts per million (volume/volume basis)
PRB	Powder River Basin
RFCS	Research Fund for Coal and Steel (EU)
SCL	syngas chemical looping
SEM	scanning electron microscopy
TGA	thermogravimetric analyser (or thermogravimetric analysis)
US DOE	US Department of Energy
Wth	watts, thermal
XRD	X-ray diffraction
YSZ	yttria-stabilised zirconia

In addition, this report makes frequent use of chemical formulae in place of chemical or common names.

Contents

1 Introduction

CO_2 capture and storage will become an integral part of large-scale coal-fired power generation systems during the coming decades. Although the first commercial installations, expected during the 2020, are likely to use post- or pre-combustion capture or oxyfuel combustion technologies to capture the gas, there are a number of less developed but potentially superior systems that should become available a little later to permit reduced costs and improved efficiencies. A promising approach uses chemical looping combustion and this report describes work in this field.

There are variations, but the common feature is that an oxygen-containing solid material, frequently a metal oxide, supplies the oxygen to a fuel, and the spent oxygen 'carrier' is separately regenerated (re-converted to its oxygen releasable form) by high temperature reaction in an air stream. The cycle is operated continuously, and arrangements for implementation can be through use of two fluidised beds, linked by oxygen carrier transport between them, or through employment of batch reactors that operate alternately in oxygen absorbing and oxygen releasing mode. Other methods are also possible. As there is no direct contact between air and fuel, CO_2 recovery is simplified, even approaching 100%, as nitrogen or excess oxygen is not mixed with the fuel reactor products. There is potential for higher efficiency in delivery of energy than for conventional combustion or gasification with 90% CO_2 capture because of this, and also because the looping reactions allow a greater thermodynamic reversibility in the conversion of the chemical energy of the fuel into heat (Jin and others, 2009). In addition, NOx emissions are low, because the temperature in the oxidation (carrier regeneration) reactor is lower than in conventional combustion flames. The fuel may be gaseous or solid, and more elaborate chemical looping systems are also a future possibility for hydrogen production.

The history of chemical looping combustion has been well summarised by Lyngfelt and others (Lyngfelt and others, 2008; Lyngfelt, 2010) and by Anthony (2008). Lyngfelt and others (2008) refer to its development from an early US patent in 1954 as a means specifically for producing pure CO_2 (Lewis and Gilliland, 1954), through the recognition of its potential value for CO_2 capture by Japanese workers under Ishida in the 1990s (Ishida and Jin, 1994), to first continuous tests by Lyngfelt and his associates at Chalmers University of Technology, Sweden, in a linked fluidised bed system in 2001. They included in their 2008 technology status paper a detailed tabulation of the primary sources of literature on oxygen carrier development.

Most of the initial tests of metal oxide oxygen carriers were on small samples in thermogravimetric analysers, and these systems are still used extensively in evaluations of potential new oxygen carriers. Batch reactors, both as fixed beds and fluidised beds, are also used for carrier tests, on samples of up to a few hundred grammes.

Researchers working on chemical looping combustion and related systems are active in a number of countries including Austria, Canada, China, Germany, Japan, Korea, the Netherlands, Russia, Spain, Sweden, the UK and the USA. In his presentation given in March 2010, Lyngfelt provided a summary tabulation of the continuous chemical looping combustors existing by that time, together with the total operating times of most of them (Lyngfelt, 2010). A 10–30 kWth installation also exists at the Thermal Engineering Institute (VTI) in Russia (Ryabov and others, 2009). Lyngfelt's table is reproduced in Table 1. The smallest continuous unit, at Chalmers, develops 300 Wth and the largest, at the University of Technology, Vienna, Austria, produces nominally 120 kWth. A 1 MWth plant has recently

Table 1 Overview of existing chemical-looping combustors (Lyngfelt, 2010)

Location	Unit	Oxides tested	Operational hours	Fuel
Chalmers, Sweden	10 kW	NiO, Fe_2O_3	1350	natural gas
KIER, Daejeon, Korea	50 kW	NiO, CoO	28	natural gas
CSIC, Spain	10 kW	CuO, NiO	140	natural gas
Chalmers, Sweden	0.3 kW	NiO, Mn_3O_4, Fe_2O_3, ilmenite	730	natural gas, syngas
CSIC, Spain	0.5 kW	CuO, NiO	660	natural gas
Chalmers, Sweden	10 kW – SF	ilmenite	90	coal, petcoke
KIER, Daejeon, Korea	1 kW	NiO + Fe_2O_3	n/a	CH_4
Vienna, Technical University	140 kW	ilmenite, NiO	390	natural gas, CO, H_2
Alstom	15 kW	NiO	100	natural gas
Nanjing, China	10 kW – SF	NiO, Fe_2O_3	n/a	Coal, biomass

been commissioned at the University of Darmstadt, Germany (Ströhle and others, 2010; Vattenfall, 2010). International collaborations have reached the point of a preliminary design for a 10 MWe gas-fuelled demonstration unit (Mattisson and others, 2009b). In fact, most tests to date have used gaseous hydrocarbon fuels, as at the Vienna pilot unit, but in some places there have been studies using solid fuels and syngas. The Darmstadt pilot plant will use coal.

Another family of solids chemical looping systems associated with CO_2 abatement that is under development uses dry regenerable CO_2 absorbing chemicals in cycles to capture it from flue gases from a conventional boiler. These carbonate looping cycles are described in the recent IEA Clean Coal Centre report: *Post-combustion carbon capture – solid sorbents and membranes* by Davidson (2009). The present report concerns solids looping systems that transfer oxygen, and the use of the term chemical looping here should be taken to refer to these systems only.

The remainder of this report is organised as follows. Chapter 2 introduces chemical looping concepts and its specific requirements. Chapter 3 describes the laboratory work to develop and test oxygen carriers. Chapter 4 describes the small- and pilot-scale continuous PDUs that are being used to establish the proof-of-concept. Chapter 5 describes other oxygen chemical looping concepts, for example hydrogen production. Chapter 6 looks at the power cycles that have been proposed and assessed for performance. Chapter 7 looks at work that has been done on the effect of fuel contaminants. Conclusions are in Chapter 8.

2 Chemical looping combustion principles

The basic principle of chemical looping combustion (CLC) is depicted in Figure 1 (Leion and others, 2008a). In the air reactor, which operates at an elevated temperature, typically 800–1000ºC, the air contacts an oxygen-depleted carrier substance, such as a partially or completely reduced oxide of a metal, and oxygen is picked up by the oxygen carrier, liberating heat. The air reactor is frequently referred to as the oxidation reactor, as it is where the oxygen carrier is reconverted to the oxidised form. Chemically, this process can be represented in various ways. The generalised equation used by Chuang and others (2008) is:

$$Me_xO_{y-1} + ½O_2 \rightarrow Me_xO_y \qquad (1)$$

where Me_xO_{y-1} represents the oxygen depleted form of the oxygen carrier (it may or may not necessarily be the pure element, depending on the selected carrier and operating conditions), and Me_xO_y represents the composition of the carrier after it has picked up oxygen. The oxygen carrier may be a single substance, such as an oxide of copper, nickel, iron, or it may consist of the absorbing substance supported on a substrate of high surface area, such as forms of alumina or silica, that does not take part in the reactions. Use of a substrate can facilitate separate optimisation of oxygen carrying capacity and mechanical strength.

In the fuel reactor (referred to frequently in descriptions as the reduction reactor, as here the oxygen carrier is reduced), also at an elevated temperature, oxygen from the carrier combines with the carbon and hydrogen in the fuel, reforming the oxygen-depleted form of the carrier. The generalised reaction shown below, is for methane fuel:

$$4Me_xO_y + CH_4 \rightarrow 4Me_xO_{y-1} + 2H_2O + CO_2 \qquad (2)$$

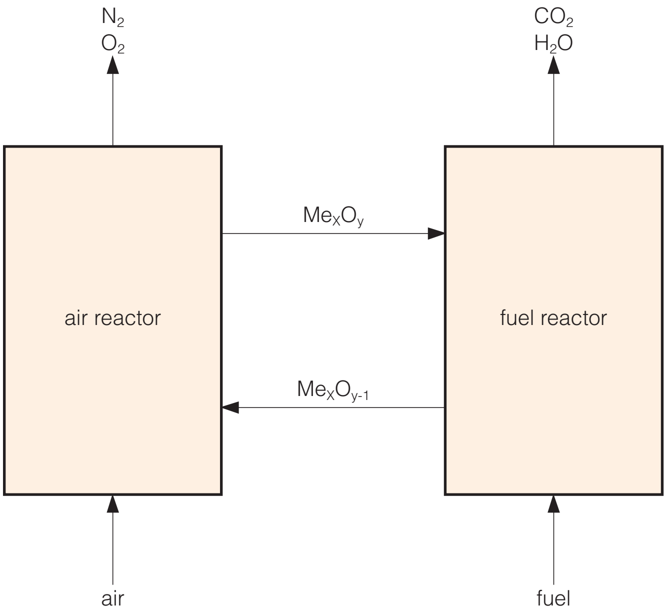


Figure 1 Basic principle of CLC (Leion and others, 2008)

The reaction in the fuel reactor can be exothermic or endothermic, depending on the fuel and the particular oxygen carrier. In the case of methane and Ni-based oxygen carriers, it is endothermic (Bolhàr-Nordenkampf and others, 2009).

For coal, represented simplistically by C_nH_m, the equivalent of equation (2) for combustion is:

$$(2n+½m)Me_xO_y + C_nH_m \rightarrow$$
$$(2n+½m)Me_xO_{y-1} + ½mH_2O + nCO_2 \qquad (3)$$

In practice this normally occurs in stages within the fuel reactor, with initial pyrolysis, followed by relatively slow char gasification, then subsequent rapid combustion of the gasification products by the oxygen carrier. The pyrolysis products will also react rapidly with the oxygen carrier. An exception to this probable mechanism occurs in so-called chemical looping with oxygen uncoupling (CLOU) systems, in which gaseous oxygen is released *before* reaction with the fuel, so that the coal is directly combusted. In normal CLC, removal of char gasification products by the oxygen carrier has been observed to increase the gasification rate, but the latter still proceeds more slowly than the subsequent reaction of carrier with the gaseous products (Leion and others, 2009c).

Appropriate physical arrangements must be provided to enable the desired reactions to proceed sufficiently far for efficient fuel utilisation and purity of the CO_2 stream to be achieved. The cyclic nature of chemical looping means that interconnected fluidised bed systems are well suited, as they can provide the necessary residence time and good solids/gas contacting for oxygen absorption and release as well as ready and efficient disengagement of the solids from the gas streams with cyclones. For solid fuels, the system design also needs to incorporate means for effective separation of ash for disposal. Figure 2 shows a process flow diagram for a solids CLC system developed within the ENCAP project by Alstom using their CFBC experience (Semedard and others, 2008).

Equation (3) shows (2n+½m) molecules of Me_xO_y reacting with each molecule of C_nH_m, by releasing (2n+½m) atoms, or (n+¼m) molecules of oxygen to each fuel molecule. The overall reaction (4) is of course the normal combustion reaction:

$$C_nH_m + (n+¼m)O_2 \rightarrow ½mH_2O + nCO_2 \qquad (4)$$

Provided oxidation of the fuel is complete and minor impurities are not present, the CO_2 stream is ready for geological storage after heat recovery and removal of the accompanying product water.

The thermodynamics and kinetics of potential oxygen carrier oxidation and reduction reactions have been the subject of many and continuing investigations. Determination and calculation of the thermodynamic quantities such as the enthalpies of the reactions allow the equilibrium constants to be calculated for different temperatures. This allows the theoretical maximum yields to be calculated. Equilibrium

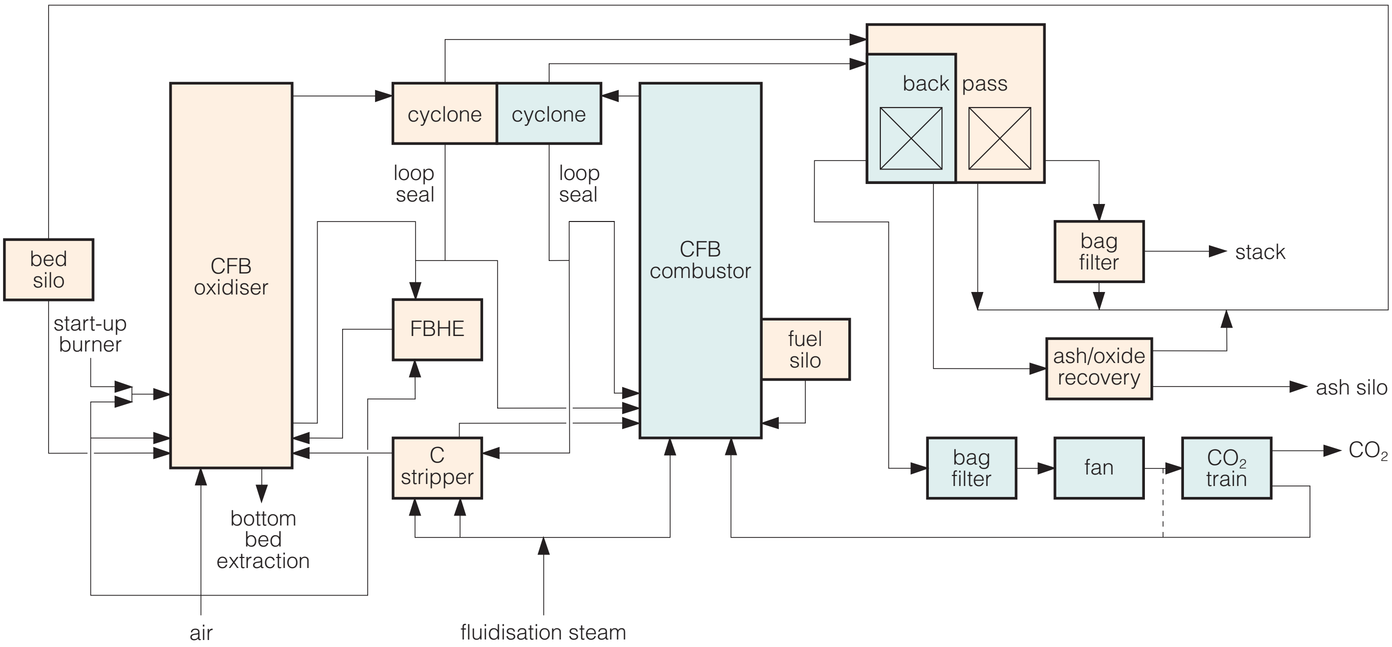


Figure 2 CLC process flow diagram (Semedard and others, 2008)

conditions may not necessarily be met, but they provide an important pointer, particularly towards eliminating potential oxygen carriers that are not favoured.

Experimental work is always necessary to determine the reaction kinetics. These provide the information needed to calculate recirculation rates and minimum solids inventories for CLC plant. Higher reactivity and oxygen transfer capacity of the carrier translate into lower inventory and recirculation rate. Tests in a continuous PDU under conditions approaching the real situation of a plant are also needed to confirm best operating conditions. These will be selected as a compromise between many factors. These include not only the need to maximise utilisation of the oxygen carrier, maximise fuel utilisation, minimise excess air supply and a host of other factors, but also to utilise heat most effectively, achieve optimum economic life of the carrier, and so on.

2.1 Examples of CLC nomenclature

Many terms are used by researchers when they characterise performance of CLC systems. Brief descriptions and comments on some of these are provided below.

The *reactivity* of a carrier is a measure of its rate of reaction for oxygen transfer. It has dimensions of time^{-1}, (for example, s^{-1} or %/min) but note that its value will vary even for a given carrier and given reaction conditions, because the reaction rate will depend on the particular fuel being combusted (Adánez, 2010).

The *rate of conversion* of the (solid) fuel similarly is expressed in time^{-1}, (s^{-1} or %/min).

The *oxygen transfer (or transport) capacity*, R_O, of a carrier is the fraction by mass of the carrier that consists of available oxygen, given by:

$$R_O = (m_{ox} – m_{red})/m_{ox}$$

where m_{ox} is the mass of the oxidised form and m_{red} the mass of the reduced form of the carrier. Among the carriers that have been extensively investigated, the pure NiO/Ni system has the highest value, at 0.214. Support materials such as forms of alumina or kaolin (an aluminosilicate) are often used in oxygen carrier preparations, and the effective value of R_O naturally decreases in consequence. Ilmenite is finding increasing favour for investigation as a carrier for coal CLC as it is a plentiful, natural material of low cost and would not require a support. It has an R_O value of 0.04, although this decreases upon continued use, while at the same time the reactivity actually increases. The oxygen transport capacity of a number of materials is shown in Figure 3 (Adánez, 2010).

The *mass-based conversion*, ω, is the mass of the oxygen carrier at any given time (m) divided by the mass of the oxidised form of the carrier (Leion and others, 2009d):

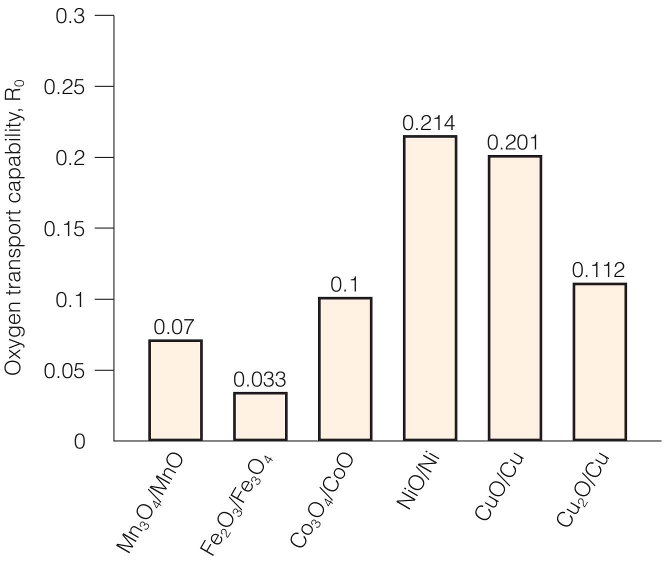


Figure 3 Oxygen transport capability of different MeO/Me systems (Adánez, 2010)

$\omega = m/m_{ox}$

The *degree of conversion of the carrier (or carrier conversion)* (X), sometimes called the *oxygen yield* or *oxygen conversion*, is the fractional extent of oxidation of the carrier at a given time:

$X = (m – m_{red})/(m_{ox} – m_{red})$

Thus,

$\omega = 1 + R_O(X-1)$

In a CLC process plant, the required *solids inventory* in the fuel and air reactors as well as the *recirculation rate* of oxygen carrier between the reactors are parameters that are linked and depend on the reactivity, oxygen transport capacity and carrier conversion. The solids inventory is often expressed as a specific value, for example kg/MWth.

3 Development and evaluation of oxygen carriers

Much of the work on chemical looping consists of developing and testing potential oxygen carriers. This section mainly reviews work published in the last three years. For the gaseous fuels, emphasis is placed on CLC research using synthesis gas, rather than methane.

An oxygen carrier needs to have the following characteristics:

- high reactivity;
- high oxygen carrying capacity to minimise solids inventories;
- ability to withstand multiple oxidation/reduction cycles while retaining high reactivity;
- ability to withstand the presence of contaminants (for example sulphur or mineral matter) while retaining reactivity;
- high resistance to attrition from mechanical, chemical and thermal stresses;
- resistance to sintering and agglomeration, which may cause deactivation or defluidisation;
- low environmental impact and non-toxicity
- low lifecycle cost.

Not surprisingly, some of these desirable characteristics can work against each other, and the best combination of physical and chemical properties is usually a compromise. A starting point in assessing potential carriers for their chemical characteristics is the determination of the thermodynamic and kinetic data for the reactions involved.

Physical and mechanical properties can be determined from tests and can be improved in many cases by using inert supports for the active constituent, nickel oxide can be supported on forms of alumina. However, where coal is the fuel, specially designed prepared carriers tend to be too expensive, and are more sensitive to deactivation by contaminants. Required make-up of carrier will be greater when using solid fuels because of:

- a higher proportion of contaminants giving greater deactivation;
- losses with ash off-take. In this case, cheaper, lower reactivity, lower capacity carriers, such as ilmenite, haematite or iron oxide waste materials, may then be preferred. They are also more likely to be environmentally benign and less toxic. The less good chemical characteristics of such materials may be compensated by increasing the solids inventory in the CLC and adjusting recycle and carbon stripping rates.

3.1 Oxygen carrier development on gaseous fuels

NiO has been most studied for methane fuel because of its high reactivity. The researchers at Chalmers University explored the preparation and use of formulations based on NiO, supported on α-alumina and other substrates for CLC of methane within the EU *CO_2 Capture Project* and the project *Chemical Looping Combustion – CLC Gas Power*. Some of the carrier preparations incorporated Ca and Mg based additives (Jerndal and others, 2009). Spray drying was used to prepare the NiO-based carriers supported on $NiAl_2O_4$ (spray drying is widely used industrially for production of particles in other applications). The spray-dried products were sintered at 1300–1600ºC. The carriers were tested for physical properties. Density was little changed by use of the additives or when $MgAl_2O_4$ was used as support, but crushing strength was usually increased. The density and crushing strength increased with sintering temperature. The carriers were tested for reaction with oxygen (5%) and methane at 950°C in a small (22 mm ID) fluidised bed reactor. The main aim of investigating the use of magnesium-containing support materials was to increase fuel conversion early in reduction. The latter is limited for NiO oxygen carriers supported by $NiAl_2O_4$, believed by the authors to be because of the limited number of metallic Ni sites. Materials with MgO were indeed found to give a considerably increased methane conversion when the oxygen carrier was highly oxidised (Jerndal and others, 2009; Linderholm and others, 2009). Related continuous tests (not all using spray dry prepared carriers) were carried out in PDUs and pilot plants at Chalmers (10 kWth), CSIC, Zaragoza (500 Wth) and the Vienna Institute of Technology (120 kWth) (*see* Chapter 4).

A large number of potential oxygen carriers (300 types) based on Ni, Mn, Cu and Fe with various supports were also prepared for screening under a joint European Coal and Steel Community (ECSC)-funded project conducted in Sweden, Spain and Austria to develop CLC technology for combustion of coal-derived syngas. This followed earlier work under other funding, such as that reported by Mattisson and others (2003) and Cho and others (2004). The ECSC project included developing a suitable reactor design and operating conditions and the construction and operation of a laboratory process development unit (PDU) to establish proof-of-concept (Mattisson and others, 2006, 2007). The tests were also relevant to direct CLC of coal.

Methods used for the oxygen carrier preparation were extrudation of mixed pastes, impregnation and freeze granulation. The first method was used for samples for initial screening, while the other methods provided selected carriers for detailed investigation. All the testing was carried out in a thermogravimetric analyser (TGA) using simulated syngas for reducing experiments and dry air for oxidation. In the initial screening, five reduction/oxidation cycles were carried out, and the carriers for detailed investigation were selected from those found to display a combination of high crushing strength and high reactivity. The detailed evaluations provided the degree of conversion of the solids (carriers) during the reduction and oxidation reactions as well as degree of conversion of fuel gas to CO_2 and H_2O. Kinetic data were also determined for some Cu, Fe and Ni-based carriers (Mattisson and others, 2007). High reactivities found for Mn, Fe and Cu oxygen carriers using CO and H_2 suggested that these cheaper and more environmentally sound metal oxides may be better candidates than the more expensive Ni carrier for syngas (but not for methane) (Mattisson and others, 2006). A manganese oxide-based carrier showed high reactivity and carrier conversion at temperatures as low as 650°C.

The kinetic data were used to calculate design criteria, such as recirculation rates and minimum solids inventories for a syngas CLC using interconnected fluidised beds. A nickel-based carrier showed a lower solids flow requirement per MW than copper or iron-based ones because of the combination of a high oxygen transport capacity of NiO and the high active metal content in the prepared carrier – *see* Figure 4, from Mattisson and others (2007). The Ni-based oxygen carrier also had the lowest required solids inventory for similar reasons. However, all three formulations would be suitable for a practical CLC system burning syngas.

In Korea, Baek and others (2009) employed spray drying to prepare a 70% NiO-based oxygen carrier in the form of spherical particles. The solid spherules were pre-dried then calcined at 1100ºC and 1250ºC. SEM imaging and porosity measurements were carried out on the prepared carriers. Resistance to attrition was determined using an ASTM method. The reactivity of the oxygen carrier (20 mg samples) for combusting simulated syngas was assessed by TGA over temperatures from 700–1000ºC. Air was used for carrier oxidation. Nitrogen was supplied between reduction and oxidation to avoid direct contact of fuel and air. At least five cyclic reduction and oxidation tests were performed and the data obtained in the fifth cycles were used for assessment.

The TGA tests showed that carbon was deposited on the carriers at 700ºC, but that no deposition occurred at temperatures above 800ºC. Although any deposited carbon was subsequently easily oxidised when air was used to regenerate the carrier, this would reduce CO_2 capture. Carbon deposition is a well-known undesirable occurrence in CLC of gaseous fuels, and needs to be minimised to prevent CO_2 'leakage' in this way. Oxygen transfer capacity increased with increase of reduction temperature, approaching its theoretical maximum of 14.7 wt% at 900ºC and 1000ºC. The overall conclusions were that the spray dry prepared oxygen carrier had physical and chemical properties indicating its suitability for use (on syngas) in fluidised bed CLC, but that it should be further developed to obtain a higher specific surface area and higher attrition resistance at lower calcination temperatures (Baek and others, 2009). Subsequent work confirmed that using a support based on γ-Al_2O_3 and pseudoboehmite (another form of alumina) enabled the calcination temperature to be lowered to 1000ºC, while retaining high attrition resistance and oxygen carrying capacity and reactivity (Baek and others, 2010a). Carriers of high capacity and strength could also be produced by mechanical mixing and extrusion and relatively low calcination temperatures using γ-Al_2O_3 support (methane fuel) (Baek and others, 2010b).

At the Korea Institute of Energy Research, Daejeon, a fluidised bed reactor (50 mm ID) was used to investigate the reduction and oxidation characteristics of four oxygen carriers for combusting simulated syngas (Ryu and others, 2009a). The preparation methods and properties of the four oxygen carrier particles used (NiO/bentonite, $NiO/NiAl_2O_4$, $Co_xO_y/CoAl_2O_4$, OCN-650) are summarised in Table 2. All the carriers showed high gas conversion (99.3–100%), high CO_2 selectivity (98.9–100%), and undetectable NOx emissions from the oxidiser. The results indicated that long-term operation was possible, although $Co_xO_y/CoAl_2O_4$

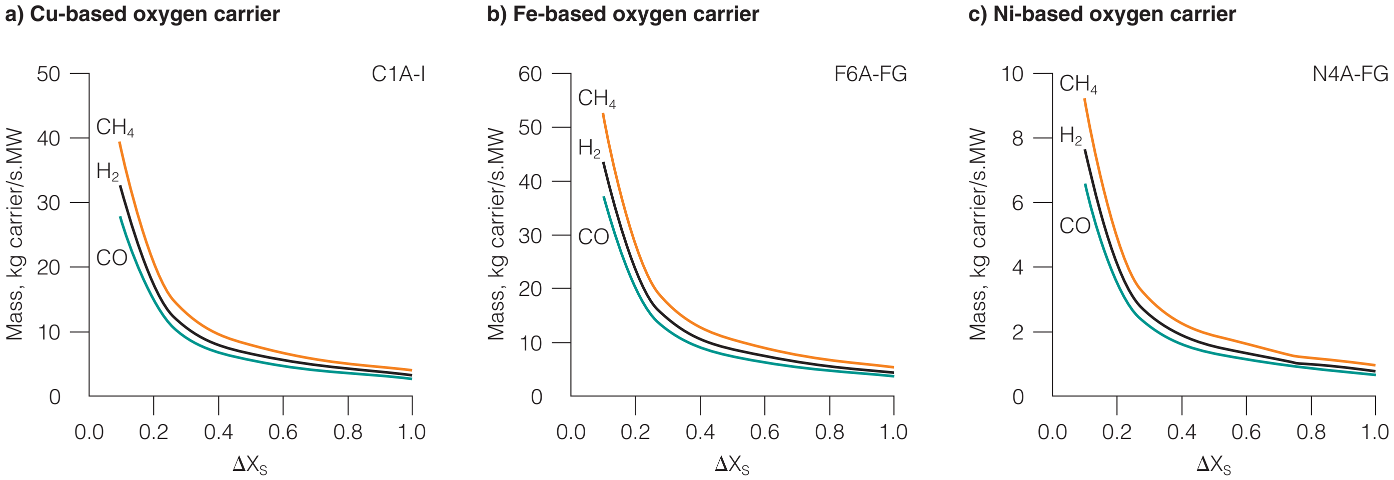


Figure 4 Calculated oxygen carrier recirculation rates for methane combustion for different oxygen carriers (ΔX_S is the difference in solid conversion between the reactors) (Mattisson and others, 2007)

Table 2 Properties and preparation methods of four oxygen carrier particles – Korea Institute of Energy Research, Daejeon (Ryu and others, 2009a)

Oxygen carrier particle	NiO/bentonite	$NiO/NiAl_2O_4$	$C_{ox}O_y/CoAl_2O_4$	OCN-650
Particle size range, µm	106–212	106–212	106–212	106–212
Metal oxide, wt%	60	70	70	60
Bulk density, kg/m³	1172	1520	1024	903
Preparation method	Mixing	Dissolution	Co-precipitation/impregnation	Spray drying

exhibited a small decay in activity as the number of cycles increased and its oxidation rate was slower.

In France, under the collaborative project CLC-MAT, Chandel and others (2008) have used a fluidised bed reactor (96 mm ID) at the Ecole des Mines de Nantes to gather data for simulation of a 30 MWth CLC system. This would use linked fluidised beds as usually envisaged (fast bed for air reactor, bubbling bed for fuel reactor). Cyclic oxidation/reduction tests (10 cycles at 800ºC, 850ºC and 900ºC) were conducted using $NiO/NiAl_2O_4$ oxygen carrier, on methane, syngas and biogas, at different temperatures, both with and without steam injection during fuel reaction. The addition of steam to the fuel reactor prevented carbon deposition with methane. An observation made by these workers was that, in a commercial plant, because a very high recirculation rate for the oxygen carrier would not be needed using Ni-based carriers because of their high oxygen carrying capacity, there might be difficulties in achieving sufficient heat transfer from air reactor to fuel reactor in cases where the fuel reaction was endothermic, as for biogas. This would not however be a problem for syngas because for that fuel the reaction is exothermic.

At the University of Cambridge, in the UK, laboratory-scale work is in progress to develop oxygen carriers for CLC of syngas as part of a coal CLC system, in which the syngas would be produced in situ from pyrolysis and char gasification (Chuang and others, 2008). Steam or CO_2 or both would first be fed to the CLC reactor. The envisaged practical arrangement for a CLC plant based on this method of operation is described in Section 3.2, where the team's work using solid fuels is discussed. Copper-based carriers supported on gamma alumina (γ-Al_2O_3) are among the oxygen carriers under investigation. Although of relatively low cost and high oxygen carrying capacity, CuO carriers can have a tendency toward agglomeration. The work at Cambridge showed that preparation methods are important for the achievement of a viable carrier. Techniques used were:

- mechanical mixing of powdered CuO with γ-alumina;
- wet impregnation of crushed γ-Al_2O_3 with $Cu(NO_3)_2$ solution, followed by heat treatment;
- co-precipitation of $CuCO_3$ and $Al(OH)_3$ from mixtures of solutions of the nitrates.

Cyclic testing of 0.5 g samples of carrier were carried out in a laboratory fluidised bed apparatus at 800ºC, using 2.5% (v) CO as fuel, alternating with air for re-oxidation, with intermediate nitrogen flush. Samples were characterised using X-ray diffraction (XRD), gas adsorption analysis and scanning electron microscopy (SEM).

Only co-precipitation produced suitable carriers. The mechanically mixed or wet-impregnated ones did not maintain high reactivity over repeated cycles because they agglomerated due to poor distribution of CuO on the support. The co-precipitated carriers had CuO and Al_2O_3 fairly evenly distributed throughout the particles. (However, note that Mattisson and others (2007) did find that impregnation did produce effective CuO-Al_2O_3-based carriers.) Careful control of alkalinity in the preparation of the co-precipitated carriers was necessary to achieve a product of adequate attrition resistance: a pH of ~9.7 produced a favourable result (Chuang and others, 2008). A later paper (Dennis and others, 2010) describes tests using a CuO-based carrier to process two coals – *see* Section 3.2.

Ilmenite ($FeTiO_3$) has been examined for use as an oxygen carrier in a fluidised bed batch reactor (55 mm ID) at Instituto de Carboquímica (CSIC), Zaragoza, Spain (Cuadrat and others, 2009) using synthesis gas mixtures. Reduction and oxidation of the pre-calcined carrier (500 g) were carried out in 20+ successive cycles, at 900ºC, with nitrogen flush separating the two steps. CO and CO_2 were not observed during nitrogen admission or oxidation, indicating that there was no carbon deposition during reaction with CO or CO_2. Figure 5 shows the CO_2 or H_2 concentration in the product gas during consecutive reduction periods. The ilmenite increased in reactivity with the number of cycles. Reaction with H_2 was faster than with CO, and near full H_2 conversion was obtained. After several cycles, reactivity stabilised and the CO_2 or H_2O concentration reached its highest value. The oxygen yield and the extent of ilmenite conversion increased during the initial reactivity rise, then stabilised (Cuadrat and others, 2009).

Ilmenite has the potential to agglomerate (*see*, for example Perrault and others, 2010), but defluidisation was only observed during oxidation when free FeO appeared during the previous reduction, a situation not expected in a practical system. Attrition was also low. An external shell on the

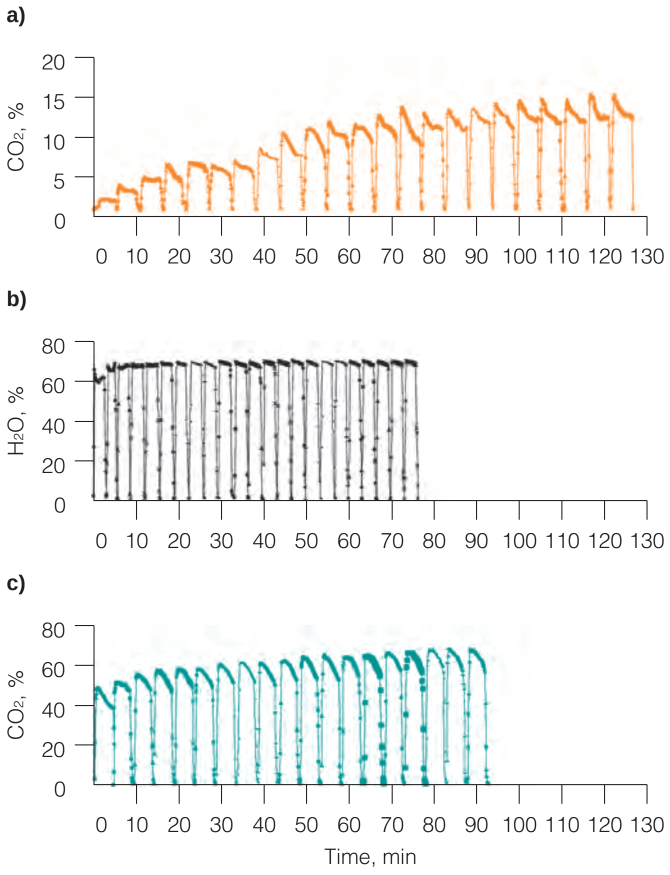


Figure 5 **CO_2 or H_2 concentrations in the product gas from batch reactor studies on a) CH_4, b) H_2 c) CO using ilmenite oxygen carrier** (Cuadrat and others, 2009)

Table 3 Characterisation of fresh, calcined, and activated ilmenite – tests at CSIC, Zaragoza (Adánez and others, 2010)

	Fresh	Calcined	Activated
XRD, main species	$FeTiO_3$, Fe_2O_3, TiO_2	Fe_2TiO_5, Fe_2O_3, TiO_2	Fe_2TiO_5, Fe_2O_3, Fe_3O_4, TiO_2
True density, kg/m^3	4580	4100	4250
Porosity, %	0	1.2	35
Particle diameter, µm	150–300	150–300	NA
BET surface area, m^2/g	0.6	0.8	0.4
Crushing strength, N	2.4	2.2	1.0

ilmenite particle surface, enriched in iron (as Fe_2O_3), was observed. This was consistent with the increase in reactivity and also with the oxygen transport capacity decreasing from an initial calculated value of 4% to 2.6%. Although there is thus a trade-off between increase in reactivity and decrease in the oxygen transport capacity, these values were judged to be within acceptable limits (Cuadrat and others, 2009).

The CSIC team are also using TGA (50 mg samples) to investigate more closely the effect of multiple reduction-oxidation cycles on the properties of ilmenite (Adánez and others, 2010). The ilmenite was pre-calcined in air at 950ºC. The familiar procedure of alternating air and reducing gases (for periods of 1–30 min for each), with intermediate flushing with nitrogen, was employed. The composition of the gas during the reduction period was 15% H_2, 20% H_2O, 15% CO, 20% CO_2, or 15% CH_4 and 20% H_2O, with N_2 balance. XRD analysis revealed that the fresh ilmenite consisted largely of $FeTiO_3$, haematite (Fe_2O_3), and rutile (TiO_2) and that calcination converted the $FeTiO_3$ to Fe_2TiO_5. The properties of these and of the material after several cycles (activated) are shown in Table 3. Reactivity increased over the first few oxidation-reduction cycles. If no pre-calcination was used, this initial build-up of reactivity was slower, and shorter reduction-oxidation periods made the total accumulated time to reach full reactivity longer.

The TGA results were used approximately to determine two design criteria for a practical CLC system: the solids inventory and the recirculation rate. The maximum economically feasible recirculation rate was 16 kg/s per MWth. The estimated inventories would be higher than for a synthetic iron-based carrier, but were considered acceptable (Adánez and others, 2010).

Ilmenite is also being tested as a carrier in Germany, at the University of Siegen, with a view to using it in a system incorporating a moving fixed bed (gravitating) reducer to process solid fuels. More information on the envisaged plant is given in Section 3.2. The tests, on 0.3 kg commercial samples of ilmenite in three size ranges (0.18–0.25 mm, 0.5–0.71 mm and 1.0–1.4 mm), used methane (diluted) in a 53 mm ID fixed bed reactor. The reduction rate of the ilmenite (based on oxygen conversion, X) varied between 0.0002 and 0.0005 s^{-1} (1.2–3%/min^{-1}) over the three particle size ranges and temperatures used (800–900ºC). At 900ºC, increasing superficial gas velocity led to an increasing reduction rate but a substantial decrease of fuel conversion. Consequently, a practical system would need to be able to accommodate increased bed height at higher gas velocities. A maximum CO_2 yield of 95% was obtained using 0.5–0.71 mm ilmenite at a temperature of 900ºC (*see* Figure 6). Agglomeration was not a problem except during the oxidation following a long-term reduction period (Schwebel and others, 2009).

In subsequent tests in the same apparatus on 0.4 kg samples of ilmenite and haematite in the same three size ranges, this time using 50% H_2, 25% CO, and 25% CH_4, diluted with nitrogen, the fine- and medium-sized samples of ilmenite had similar reaction rates, the coarser fraction showing a lower rate. For haematite, the particle size seemed to have less influence. The maximum CO_2 yield was >0.9 for ilmenite but only 0.85 for haematite. The maximum reduction rate (this time based on mass-based conversion, ω), increased over the first cycles using ilmenite, then settled down. In contrast, for haematite, the rate *decreased* over the first few cycles, before stabilising (Schwebel and others, 2010).

At Chalmers University, Sweden, a small batch fluidised bed apparatus is being used to examine a range of low-cost iron-based carriers, using simulated syngas as fuel. This has allowed a standardised technique to be employed for readily assessing key characteristics of candidate carriers for direct coal CLC, including reactivity, chemical changes, morphology and physical strength of the materials. The results have been used to predict performance with solid fuels, including required inventory (Jerndal and others, 2010). The carriers tested were six oxide scales (a by-product from hot rolling of steel) from Scana and Sandvik, an unspecified industrial iron material from Höganäs, an unprocessed iron ore from LKAB, and a material obtained from vehicle recycling from Stena Metall (‘magnetic fines’). All contained Fe_2O_3 after an initial heating in air for 24 hours, and all possessed a greater crushing strength than ilmenite, which was used as a reference carrier. Cycles of partial reduction followed by total oxidation were performed. The materials converted between 40% and 80% of the CO to CO_2, compared with 25% for ilmenite. The conversion of H_2 was >90% during most of the reduction period for all materials (generally somewhat higher than for ilmenite). Only one of the materials gave any agglomeration (the industrial iron material from Höganäs). Two of the oxide scales, from

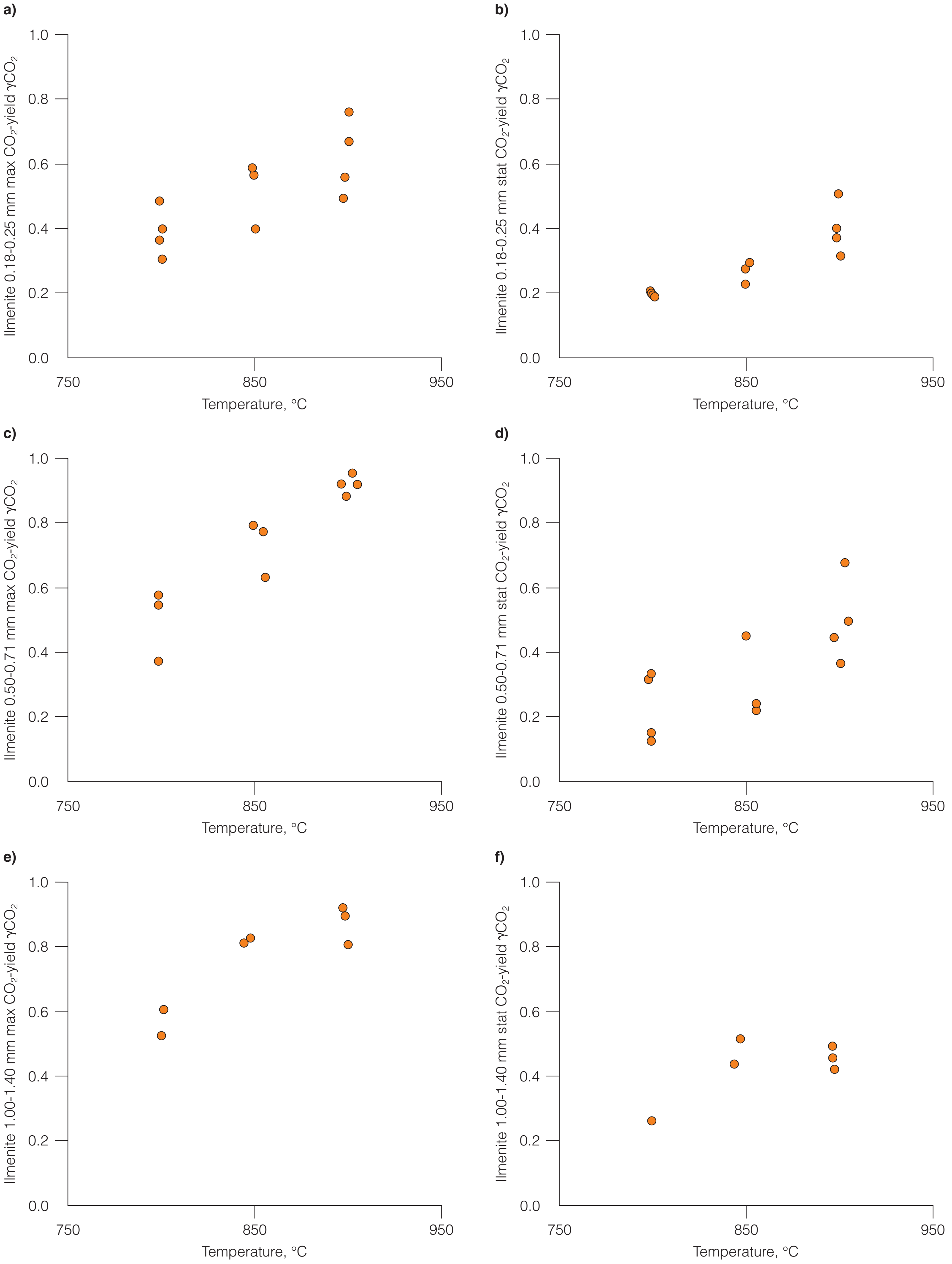


Figure 6 Maximum and stationary CO$_2$-yield (γCO$_2$) as a function of temperature for ilmenite oxygen carrier in a fixed bed reactor – methane fuel (Schwebel and others, 2009)

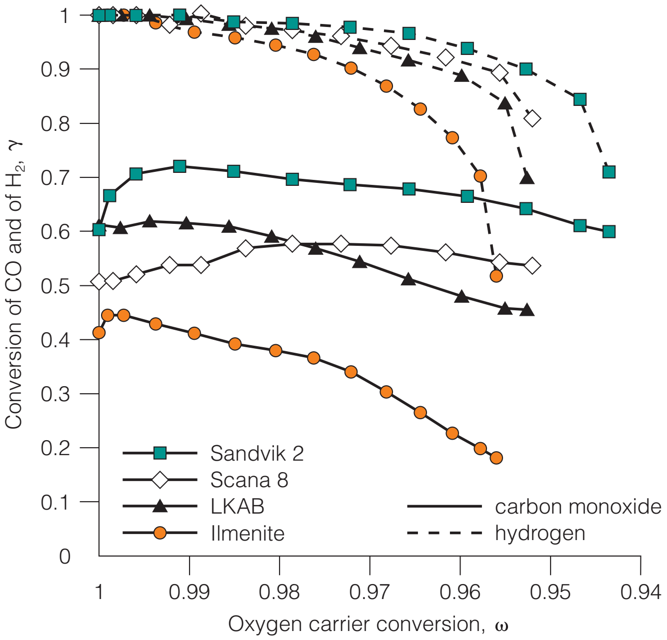


Figure 7 Conversion (γ) of H_2 and CO as a function of oxygen carrier conversion (Jerndal and others, 2010)

Sandvik and Scana, and the iron ore from LKAB were subsequently tested over longer periods because the first two had a slightly higher fuel conversion than the other carriers, while the material from LKAB showed superior reactivity and higher strength and also contained less impurities. Figure 7 shows the conversion (γ) of CO and of H_2 as a function of oxygen carrier conversion (ω) from these longer tests. The most reactive oxide scale was found to contain nickel, and it was speculated that this may have contributed to its higher conversion of the syngas. There was also evidence that softer and more porous oxygen carriers gave higher syngas conversion (Jerndal and others, 2010). Work with ilmenite, iron ore and oxide scale on solid fuels using the same apparatus is described in Section 3.2.

At Western Kentucky University, Rubel and others (2009) tested a number of oxygen carriers using reducing gas mixtures containing H_2, CO and CO_2. The aim was to explore their potential for processing coal. Repeated oxidation-reduction cycles were conducted in DSC-TGA-MS apparatus. Among the carriers investigated were commercial NiO, Fe_2O_3, CoO, and CuO as well as catalysts based on NiO, iron and iron oxides and wustite. Agglomeration was a common problem with the metal oxide powders except for Fe_2O_3, which retained its reactivity through multiple cycles. Samples which had agglomerated were solid masses with no evidence of porosity, whereas the Fe_2O_3 powder was after use found to be a single sponge-like mass with visual evidence of macro-porosity. Iron-based carriers were therefore investigated further using a char as fuel (*see* Section 3.2).

3.1.1 Mixed oxide carriers

Use of more than one active material may allow the formulation of improved, more robust carriers.

Mixed Fe/Mn oxides are being investigated at IFP, Lyon, France (Lambert and others, 2009). Small (65 mg) tests of prepared samples were conducted in a TGA in five reduction/oxidation cycles using (25%) methane, alternating with dry air for oxidation, separated by inert flushing. However, these tests and characterisation of the carriers did not indicate any obvious advantage over NiO-based carriers.

Under the CLCMAT project in France, mixed carriers based on Fe/Mn and Cu/Mn oxides have been tested. Agglomeration was found to be a problem for many of the formulations, but one, $Cu_{0.95}Fe_{1.05}AlO_4$, was stable in that respect. However, calculations showed that its reactivity (with methane) was not sufficiently high to achieve an acceptable reactor size for a commercial 120 MW natural gas-fired boiler (Rifflart and others, 2010).

In Poland, workers at the Institute for Chemical Processing of Coal, Zabrze, prepared mixed carriers based on Fe_2O_3-MnO_2 supported on ZrO_2 and Fe_2O_3-MnO_2 supported on sepiolite, for testing at the US DOE's National Energy Technology Laboratory (NETL), Morgantown (Ksepko and others, 2010a). Such carriers would have low production costs. Both materials performed well in five-cycle TGA tests on 100 mg samples, but the extent of reduction and oxidation and the reaction rates were greater for sepiolite. The TGA tests also showed that H_2S in the fuel gas (H_2 and CO) did not affect oxygen carrying capacity or reaction rate for either support. Multiple cycle oxidation/reduction tests were also carried out on the ZrO_2-supported carriers using a bench-scale fixed bed reactor using simulated syngas at 800ºC. These showed complete combustion of H_2 and CO. XRD analysis showed no formation of sulphides, sulphites or sulphates. Tests using NiO on various supports have also been reported and sepiolite appeared promising for supporting this carrier also (*see* Chapter 7).

At the University of Newcastle, Australia, physically mixed oxides of Cu(II)/Fe(III), Cu(II)/Ni(II) and Fe(III)/Ni(II) on alumina support were compared in performance with the single oxides on alumina in a series of reduction experiments using a TGA. This is part of a wider study of their reduction and oxidation characteristics. The reducing gas used consisted of mixtures of H_2, CO and CH_4 in argon. It was found that the conversion times of the physically mixed binary metal oxide particle systems were geometric averages of the conversion times of the parent materials (Moghtaderi and others, 2010).

Iron-nickel carriers are also being investigated by VTT, in Finland, with methane as fuel. Ni-addition to Fe_2O_3 appeared to increase its reactivity (Lagerbom and others, 2010). The effect was also observed in 120 MWth tests using methane fuel at the Vienna University of Technology (Mayer and others, 2010).

The use of Co in promoting Ni carriers is being investigated at the University of Western Ontario, London, Canada (Quddus, 2010). A lanthanum-stabilised alumina support was used for the carrier. Small fluidised bed tests showed the formation of easily reducible nickel oxides species through a lower formation of non-reactive nickel aluminates.

In China, at the Institute of Engineering Thermophysics, Beijing, a mixed carrier consisting of NiO and CoO supported on YSZ has been produced that performs well, with a high reactivity on methane without carbon deposition. The micro-structure after ten oxidation/reduction cycles was similar to that of the fresh material, showing a promising stability compared with that observed for single metal oxides (Jin and others, 2009).

3.2 Oxygen carrier development on solid fuels

The application of chemical looping combustion to coal for CO_2 capture was tested using iron oxide (Fe_2O_3) ten years ago by Lyon and Cole (2000). Since then, there has been slowly growing activity in the field. Progress has been slower than for the 'easier' fuel methane, and the majority of CLC testing related to coal has been on syngas. Gasifying the coal separately can ease the potential difficulties from achieving efficient fuel utilisation and separation of contaminants, but introduces its own complications. Some of the syngas CLC work described in Section 3.1 is aimed at understanding better the direct CLC of coal, which occurs via devolatilisation and gasification in the fuel reactor. Direct CLC of coal has reached proof-of-concept in small continuous units (*see* Chapter 4) and recent accompanying activity on carrier development is reviewed here.

Leion and others (2008a), at Chalmers University of Technology, Göteborg, Sweden, used a laboratory fluidised bed batch reactor to investigate the feasibility of using CLC for processing solid fuels, including petroleum coke and a number of coals possessing a range of ash and volatile matter contents. The fuel analyses are shown in Table 4. The reactor, shown in Figure 8, was shaped to ensure particles were not elutriated. The oxygen carriers were $Fe_2O_3/MgAl_2O_4$, prepared by freeze granulation then sintering at 1100ºC, and natural ilmenite ($FeTiO_3$), heat treated at 950ºC. The batch reactions involved steam gasification in the presence of the oxygen carrier (40 g) at temperatures of 850–1000ºC, alternating, after a nitrogen flush, with introduction of 'air' containing 5% O_2 to control temperature rises. The solid fuel (0.2 g) was introduced from the top of the reactor at the start of the reducing period. The carrier was initially heated in an inert atmosphere and then in the 5% O_2 atmosphere. Two to six reduction-oxidation cycles were carried out. Gas samples for analysis were taken during the reducing period from some of the cycles. Main parameters studied were the temperature, proportion of steam fed with nitrogen for the fuel gasification/combustion stage and fuel volatile matter content. First tests on a solid fuel (petroleum coke) in the same apparatus (using the 60% Fe_2O_3 and 40% $MgAl_2O_4$ carrier) were reported by the team in 2007 (Leion and others, 2007).

Figure 9 and Table 5 show some of the results (Leion and others, 2008a). The work confirmed that it is possible to use chemical looping for solid fuels. Agglomeration was not a problem, and the two oxygen carriers exhibited similar rates of reaction. Ilmenite (the less expensive material) was demonstrated to be usable for over 45 hours. At 950ºC, 95% conversion of fuel particles was achieved in 4–15 minutes. The gasification of the fuel (more precisely, char gasification) was the rate-limiting process, for all the solid fuels tested. A

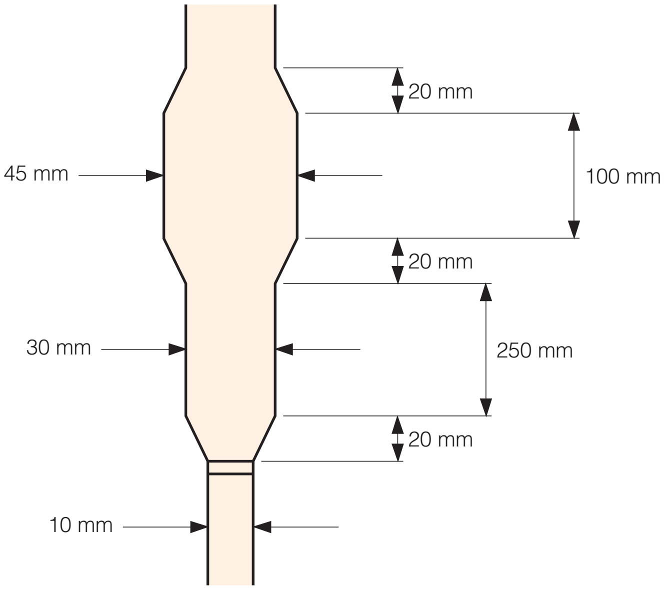


Figure 8 Laboratory fluidised bed reactor used for CLC tests on solid fuels at Chalmers University (Leion and others, 2008a)

Table 4 Analyses of solid fuels used in CLC tests at Chalmers University, Sweden (Leion and others, 2008a)

	Petroleum coke	South African coal	Chinese coal	Indonesian coal	Taiwanese coal	S France	
						Raw	Sieved
Volatile matter, %	10.0	21.6	8.8	45.3	31.5	25.0	25.0
Moisture, %	8.0	8.3	1.0	8.5	2.5	1.5	1.5
Ash, %	0.5	15.9	21.0	1.4	12.3	21.8	21.8
HHV, MJ/kg	31.7	29.9	26.6	26.4	27.9	24.9	24.9
C, %	81.3	62.5	70.3	66.1	70.6	63.9	63.9
H, %	2.9	3.5	2.8	4.7	4.5	3.6	3.6
S, %	6.0	0.7	0.6	0.1	0.5	0.8	0.8
N, %	0.9	1.4	1.1	0.7	1.7	0.8	0.8
O, %	0.5	7.7	3.1	18.5	7.9	7.7	7.7

Table 5 Reaction times (in minutes) to 95% and 80% conversion for various solid fuels and oxygen carriers – tests at Chalmers University, Sweden (Leion and others, 2008a)

	Conversion, %	Petroleum coke	South African coal	Chinese coal	Indonesian coal	Taiwanese coal	S France	
							Raw	Sieved
$Fe_2O_3/MgAl_2O_4$	95	15	9.9	13.7	5.1	11.9	9.6	8.5
Ilmenite	95	14.1	10.8	13.4	4.2	9.6	10.7	9.8
Sand	95	38.0	18.8	29.9	10.3	22.9	21.3	16.3
$Fe_2O_3/MgAl_2O_4$	80	10.8	4.1	8.5	1.5	6.0	4.6	4.0
Ilmenite	80	10.0	5.0	8.2	1.2	4.9	4.7	4.9
Sand	80	28.7	10.7	17.6	3.2	14.4	13.1	8.8

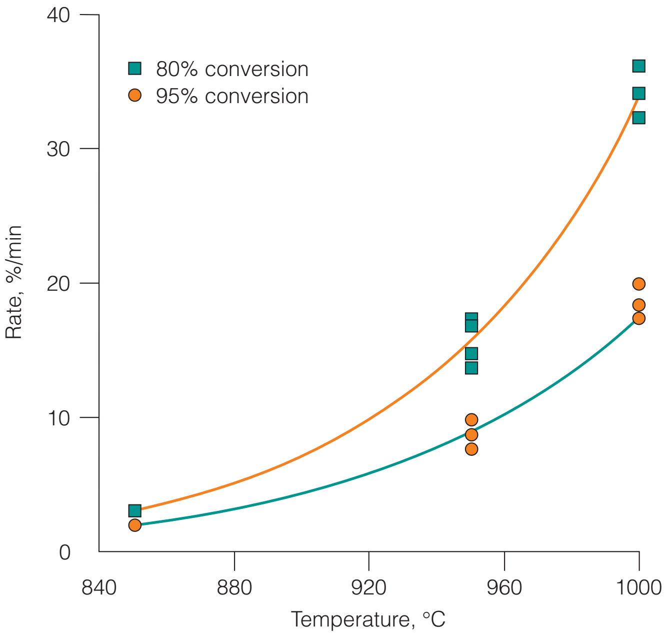


Figure 9 CLC tests of South African coal with ilmenite – average reaction rate to reach 80% and 95% conversion (Leion and others, 2008a)

higher temperature or a higher steam fraction in the fluidising gas increased the conversion rate, but high solids inventories may nevertheless be needed for practical systems. Reactive coals with high volatile matter contents, such as the South African or Indonesian coals tested, would need shorter residence times and smaller solids inventories than low volatile, less reactive solids.

The lifetime of the oxygen carrier in a continuous plant will be affected by any deactivation by the mineral matter present in the coal as well as the efficiency of ash separation. However, no deactivation was observed in these tests. Although the total conversion and conversion rate were regarded as satisfactory, generally at least 10% of the carbon was released as CO, that is it was not all converted to CO_2. Berguerand and Lyngfelt (2008a,b) have suggested the possible need for an ‘oxygen polishing’ step in a CLC plant, whereby oxygen would be injected into the gas flow exiting the fuel reactor cyclone of a CLC, to convert the residual CO to CO_2.

Further tests in the same apparatus, using an analogous experimental procedure over four to five reduction/oxidation cycles, were also carried out to explore two other low cost materials as oxygen carriers, for exapmple Mount Wright iron ore and oxide scale from steel production (Leion and others, 2009c). The fuels were a petroleum coke, charcoal, lignite and two bituminous coals (*see* Table 6). The two candidate carriers had previously shown good performance with gaseous fuels (Leion and others, 2009b). Both solids were effective as oxygen carriers and fluidisation behaviour was good. The reaction rates to 95% conversion are shown in Table 7. The oxide scale gave a more complete conversion of fuel to CO_2 and H_2O compared to the iron ore and the previously tested ilmenite. However, for all three, treatment of fuel reactor outlet gases would be needed for conversion of residual CO and H_2 to CO_2. Experiments over 40 cycles using a 50:50 CO/H_2 fuel mixture showed that the reactivities of both increased with time. It was commented that the heat balance of any magnetite based oxygen carrier, such as the oxide scales or iron ore used would be less favourable than that of ilmenite, so the required solid inventory for the CLC could be smaller for the latter (Leion and others, 2009c).

Investigations of CLC of coal using CuO, Fe_2O_3, Co_3O_4, NiO, and Mn_2O_3 are being conducted with a TGA and in a small laboratory fixed bed apparatus at the US DOE’s National Energy Technology Laboratory (NETL), Morgantown, WV, USA. The coal used for the work reported recently was Illinois No 6 (analysis in Table 8) (Siriwardane and others, 2009). Stoichiometric mixtures of the oxides with the coal were used in the TGA. The nominal mass of each mixed sample in the TGA was 150 mg, and nitrogen or CO_2 was introduced as the temperature was increased to 900–1000ºC at 15ºC/min, for about 60 min. After a further 60 min at the maximum temperature, air was introduced for 60 min. The fixed bed apparatus took 1 g samples and was linked to a mass spectrometer (MS) for gas analysis. It was used to investigate the CuO/coal mixture only.

Table 9 shows some of the results from the TGA experiments. The lowest combustion reaction temperature (700°C) and the highest combustion rate were observed for the CuO-coal system. Combustion must proceed sufficiently rapidly in a CO_2 atmosphere for a practical CLC system, and Figure 10 shows the reaction rate curve for combustion using CuO, in a CO_2 atmosphere. The rate, peaking at 0.08–0.1 min^{-1}, was not

Table 6 Analyses of solid fuels used in CLC tests at Chalmers University, Sweden, using iron ore and oxide scale (Leion and others, 2009c)

Fuel	HHV, ar, MJ/kg	Proximate analysis, % ar			Volatile matter, % daf	Ultimate analysis, % daf				
		Moisture	Ash	Combustibles		C	H	N	S	O
Mexican petcoke	30.9	8.0	0.5	91.5	10.9	88.8	3.1	1.0	6.6	0.5
Indonesian coal	25.1	8.5	1.4	90.1	45.3	73.7	5.2	0.8	0.1	20.5
Colombian coal	27.9	3.3	5.2	91.5	40.4	80.9	5.5	1.5	0.7	11.6
German lignite	20.9	10.2	5.0	84.8	50.4	69.9	5.4	0.6	1.0	23.1
Swedish wood char	–	3.0	3.0	–	11.0	83.0	–	–	–	–

Table 7 Reaction rates of iron ore and oxide scale oxygen carriers with solid fuels (%/min) – tests at Chalmers University, Sweden (Leion and others, 2009c)

Fuel	Mt Wright iron ore	Oxide scale	Ilmenite
German lignite	61.3	67.9	67.9
Colombian coal	9.4	13.1	9.4
Indonesian coal	16.6	22.7	20.2
Mexican petcoke	7.4	8.2	8.8
Swedish wood chips	–	37.3	–
Swedish wood char, 900°C	3.4	4.2	–
Swedish wood char, 950°C	8.5	–	–
Swedish wood char, 970ºC	12.7	16.8	15.1
Swedish wood char, 1000ºC	21.0	23.5	–

Table 8 Analysis of Illinois No 6 coal used in chemical looping experiments at US DOE National Energy Technology Laboratory, Morgantown (Siriwardane and others, 2009)

	wt%
Moisture	7.44
Volatile matter	37.97
Ash	12.45
H	4.63
C	67.32
N	1.3
S	4.81
O	9.49

Table 9 Reaction properties of coal CLC with various metal oxides – tests at US DOE National Energy Technology Laboratory, Morgantown (Siriwardane and others, 2009)

	Gaseous medium	Combustion				Oxidation		
		Temperature, ºC	Rate, min^{-1}	Combustion, %	ΔH, kJ/mol	Rate, min^{-1}	Oxygen uptake, %	ΔH, kJ/mol
CuO (5 µm)	CO_2	703	0.098	100	–96.5	0.172	98.6	–156
	N_2	708	0.083	100			0.175	99.2
CuO (63 µm)	N_2	780	0.079	100	–96.5	0.174	99.2	–156
NiO (44 µm)	CO_2	993	0.061	73.05	75.2	0.84	77.5	–327.7
	N_2	1000	0.017	68.4		0.82	71.6	
Fe_2O_3 (44 µm)	CO_2	973	0.055	94.9	79.2	0.77	93.7 Fe^{II}	–347.4
	N_2	977	0.05	91.6		0.78	90.6 Fe^{II}	
Mn_2O_3 (44 µm)	CO_2	905	0.011	76.76	–36.1	0.42	72.2 Mn^{II}	–216.4
	N_2	978	0.01	71		0.38	68.3 Mn^{II}	
Co_3O_4 (70 µm)	CO_2	781	0.096	83.3	–8.6	1.74	78.2 Co^{II}	–243.9
	N_2	781	0.096	83		1.74	78.0 Co^{II}	

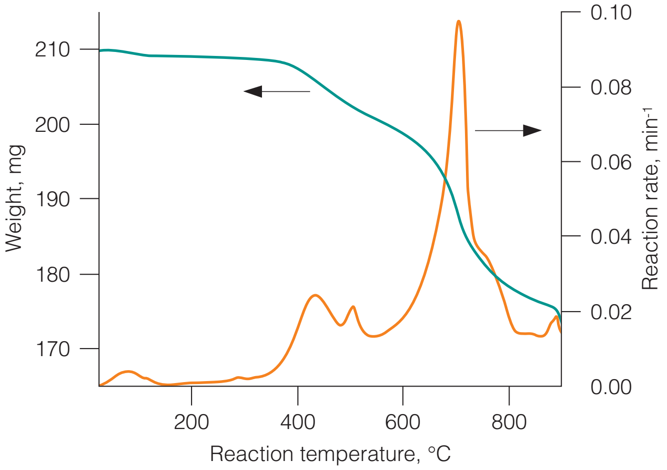


Figure 10 Reaction rate curve for CLC of Illinois No 6 coal using CuO in a CO_2 atmosphere (Siriwardane and others, 2009)

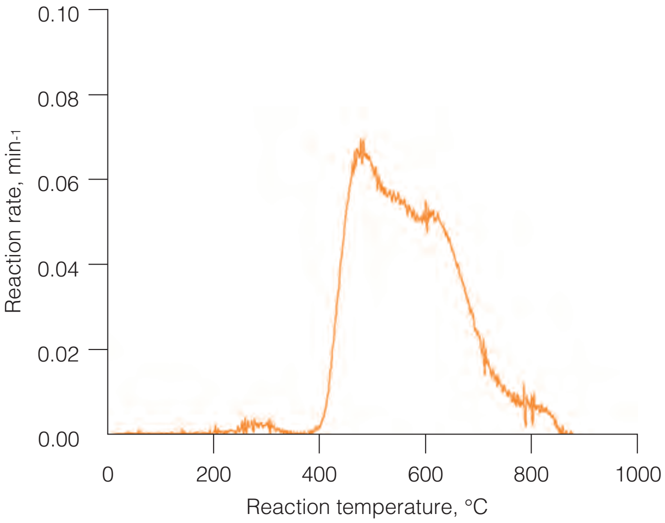


Figure 11 Reduction of CuO with carbon (Siriwardane and others, 2010a)

significantly different in N_2 or CO_2. The oxidation reaction rate was also appreciable at 700ºC. The mass changes indicated that the coal was completely combusted by the CuO carrier and that the latter was subsequently fully re-oxidised. The fixed bed experiments confirmed this and showed that no CO was produced. Repeated reduction-oxidation cycles in the TGA showed that the extent of combustion gradually decreased, reaching 68% at the eighth cycle. This was attributed to ash accumulation, which would not occur in a commercial plant. It was observed that (undesirable) reactions between ash and metal oxides, although thermodynamically feasible, could be very slow (Siriwardane and others, 2009).

Siriwardane and her team at NETL have recently reported some interesting findings from separate TGA studies of CuO in combusting coal (Illinois No 6), char, and carbon (Siriwardane and others, 2010a,b). In the generally accepted view, the coal is initially pyrolysed, releasing gaseous products and leaving a char. The char is gasified relatively slowly in the CO_2/steam atmosphere to form CO and H_2, which then react rapidly with the oxygen carrier. The pyrolysis products should also react rapidly with the oxygen carrier. In these tests, Siriwardane and her co-workers showed that a mixture of carbon and CuO, when heated in N_2, underwent reaction at a significant rate at temperatures as low as 480ºC (*see* Figure 11). As pure carbon was used, this combustion could clearly not have occurred via release of volatiles, and separate experiments without CuO present confirmed that of CO_2 did not gasify the carbon at such low temperatures. Tests in the presence of steam were not reported. The temperature at which this reaction was observed was also much lower than the temperature for decomposition of CuO when heated alone in an inert atmosphere (which was confirmed to occur at above 800ºC). When CuO particles were heated with coal, the reaction temperatures increased with increasing particle size of either carrier or coal and also if diluted with quartz powder. The conclusion from these and other tests was that the carbon-containing fuel somehow facilitated the release of the oxygen by the carrier. XRD analyses indicated that the carbon combustion started when CuO was converted to Cu_2O at around 450ºC, and that this reaction proceeded until Cu_2O was converted to the metal (Siriwardane and others, 2010a). Work reported in the latest paper indicates that carbon appears to facilitate the breaking of the Cu-O bond in CuO to produce a substantial amount of reactive oxygen. There was also evidence of surface melting of Cu and adherence to carbon particles, and it was speculated that this may facilitate the continuance of reactions through the bulk material (Siriwardane and others, 2010b).

In China, Gao and others (2008) at Southeast University, Nanjing, used a fluidised bed reactor to examine the CLC of a Chinese bituminous coal (Shenhua). The oxygen carrier, NiO supported on gamma alumina (γ-Al_2O_3), was prepared by impregnation of the support with nickel nitrate solution followed by thermal decomposition then calcination. As reported by Leion and others (2008a), the gasification reactions proceeded more slowly than the combustion of the product gases with the oxygen carrier, and the rate of conversion of fuel increased with increases in the fraction of steam in the fluidising medium and in temperature. Also analogous to Leion and others' (2008a) results, residual CO in the product CO_2 was a feature because of some of the fuel being gasified within the upper levels of the fluidised bed, so some CO escaped from the fluidised bed before it had time to contact the oxygen carrier. Work by the same team in China using two continuous PDUs, both incorporating spouted fluidised bed fuel reactors to reduce CO losses, is described in Section 4.2 and Chapter 7.

The Nanjing team are also exploring the use of CLC for coal combustion at elevated pressure using iron ore as carrier. Operation of both oxidiser and reducer vessels at pressure could allow several possible advantages, such as improved fuel utilisation in the fuel reactor and incorporation of a combined cycle power generation scheme. The proposed combined cycle is described in Chapter 6. Again, use of a spouted fluidised bed fuel reactor is envisaged, but laboratory work is initially being carried out in a fixed bed reactor of 30 mm ID, using 40 g samples of carrier. Pressures of 0.1–0.6 MPa were used. The temperature was 970°C. 0.4 g samples of coal (Chinese Xuzhou bituminous, 0.125–0.180 mm) were added to the carrier bed after a flow of 87% nitrogen+steam had been introduced. 5% O_2 in N_2 was used for the subsequent oxidation of the carrier, with N_2 introduction between these treatments. Steam gasification in the absence of carrier was also carried out as a control. It was found that increased pressure produced higher CO_2 yields and lower fractions of CO, CH_4, and H_2. The carbon conversion increased from 75.4% at 0.1 MPa to 82.9% at 0.4 MPa. Oxygen carrier conversion initially increased with pressure but decreased at pressures above about 0.5 MPa (Song and others, 2010).

Similar fixed bed reactor tests were also carried out over 20 reduction-oxidation cycles using an iron ore from Brazil, calcined at 1100ºC, and shown to consist of 94.79% Fe_2O_3, 4.31% SiO_2, and 0.91% Al_2O_3 (Xiao and others, 2010). Again, steam gasification in the absence of carrier was carried out as a control. This showed that pyrolysis occurred over some minutes, while char gasification was slower. Pyrolysis was suppressed by pressure, while char gasification was increased, resulting in higher carbon conversion within certain pressure conditions. The average carbon conversions at 0.1 MPa and 0.5 MPa were 76.48 and 84.65%, respectively. The oxygen carrier reactivity appeared to increase with each cycle. SEM showed that the iron ore particles became more porous and there was only slight sintering at elevated pressure, with no apparent agglomeration. The CO_2 fraction increased from 80% to approximate 90% after ten cycles at atmospheric pressure, while, at elevated pressures, the stable average CO_2 fraction was higher, at 95.75%. More oxygen was consumed by the reduced oxygen carrier at elevated pressure, suggesting that the depth of reduction was increased (Xiao and others, 2010).

Laboratory investigations of use of CuO oxygen carriers for combusting Powder River Basin (PRB) subbituminous coal (and two opportunity fuels), were conducted at Western Kentucky University, Bowling Green, USA (Cao and others, 2006b). Another paper described a conceptual system for applying the technology, based on circulating fluidised beds and encompassing three loop seals (Cao and Pan 2006a) (*see* Figure 12). An earlier paper had introduced the proposed design (Cao and others, 2004). Consideration of the thermodynamic and physical properties of various candidate oxygen carriers led to the selection of CuO as the best to use in practice.

The tests on the reduction of CuO by PRB coal were conducted using differential scanning calorimetry (DSC) and TGA, with a mass spectrometer connected for the characterisation of the gaseous products. Small fixed bed tests were also carried out to provide solid samples for characterisation by XRD and scanning electron microscopy (SEM). Reference tests on CuO alone were also conducted. Earlier tests on CuO with an unspecified coal using DSC and TGA showed that temperatures below 900ºC were best to limit carrier melting (Cao and others, 2005). The later work indicated that CuO can be fully converted into Cu, either in a

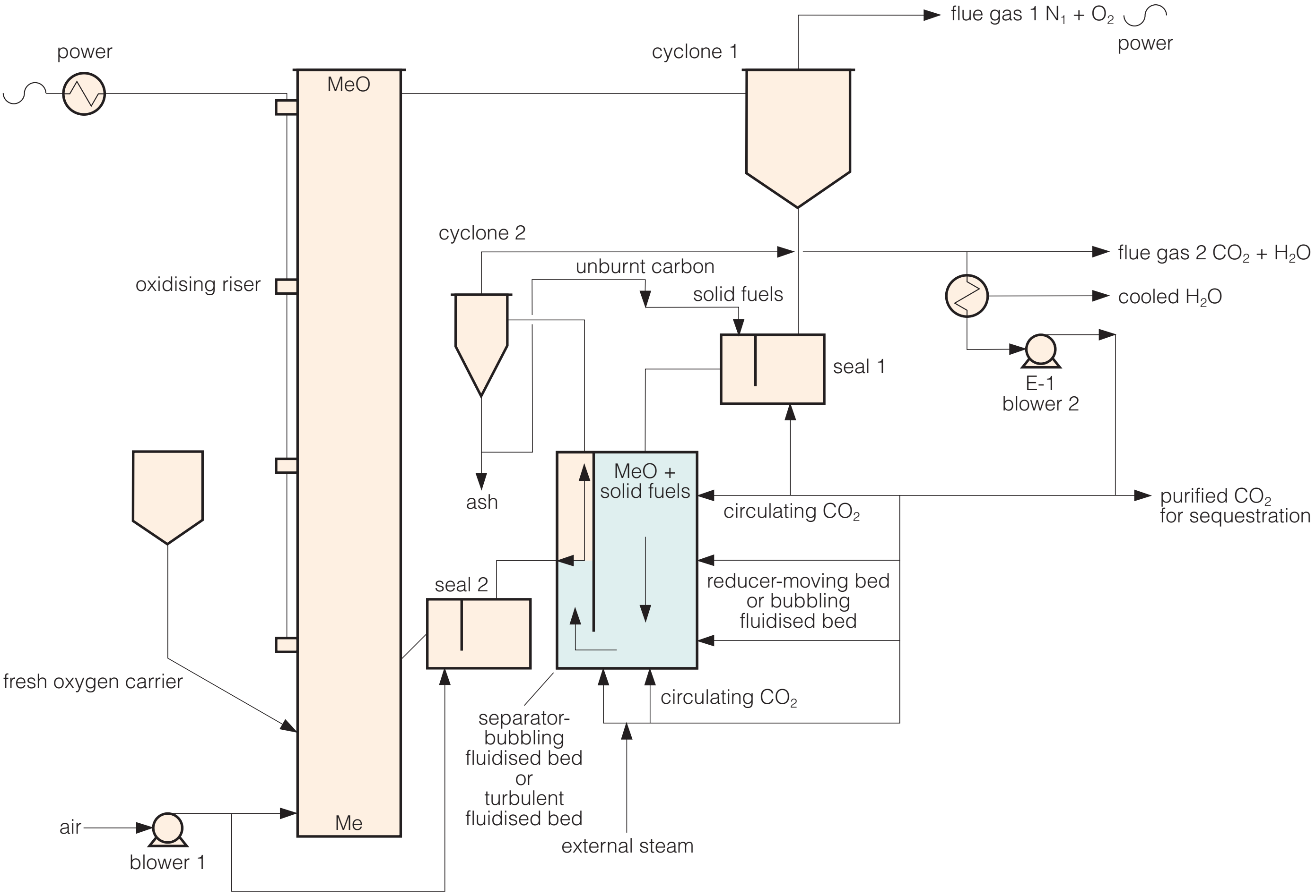


Figure 12 CLC configuration using circulating fluidised beds and encompassing three loop seals (Cao and Pan 2006a)

direct path by solid fuels, or in an indirect path via pyrolysis and gasification products. The fixed bed tests showed that a reaction time of only 15 min was sufficient for CuO to be totally reduced by the PRB coal in a CO_2 atmosphere at 800°C. This reaction time was deemed suitable for the application of a bubbling fluidised bed as reducer (Cao and others, 2006b).

Also at Western Kentucky University, Rubel and others (2009) tested the oxidation of a gasification char with Fe_2O_3 and the oxidation of a char/Fe_2O_3 mixture with added fly ash. This showed that up to 73% of the char carbon was combusted in 30 min, with up to 88% combusted after 48 h. However, more than twice the stoichiometric quantity of oxidant was needed to achieve this best result. Addition of fly ash decreased the utilisation efficiency, but still up to 73% of the carbon was combusted (Rubel and others, 2009). Subsequently, cycled reduction-oxidation tests with two iron-based carriers (fused iron − largely Fe_3O_4 – and wustite – FeO) in a TGA-MS were used to determine the effect of different concentrations of ash incorporated with the char. These showed that ash was not detrimental to the activity of the oxygen carriers (Rubel and others, 2010).

At the University of Cambridge in the UK, a coal CLC process is under development that would use batch fluidised bed reactors that would be switched from 1) gasification of a continuously fed coal, plus oxidation of the syngas by the oxygen carrier, to 2) a stage in which the fuel feeding is ceased and the remaining char is allowed to gasify to completion, to 3) a final stage, in which the fluidising gas is switched to air for re-oxidation of the carrier. Parallel reactors would be operated out of phase with each other to achieve a continuous output of energy. The advantages suggested over interconnected fluidised bed systems are that it would avoid the need for separation of unreacted carbon from the oxygen carrier and reduce mechanical degradation of the carrier. Laboratory fluidised bed tests are being conducted on a char produced from a German lignite (Hambach), using ilmenite as an oxygen carrier. The test results and results from gasification have been used in modelling the processes occurring, and agreement of experimental and theoretical results was achieved. The modelling should facilitate minimising carbon accumulation and maximising CO_2 capture (Brown and others, 2010).

The principle of the process has also been tested with a CuO carrier on alumina, prepared by impregnation, using two bituminous coals (Illinois No 5, from the USA and Taldinskaya, from Russia) and Hambach lignite (Dennis and others, 2010). The equipment included a 78 mm ID fluidised bed reactor and FTIR for analysis of samples of the product gas. The fuel was fed manually in batches to the top of the bed, as an installed automatic feeder gave unstable flow rates in these small-scale experiments. The sequence of reactions showed that the lignite was gasified completely by 15 mol% CO_2 in N_2 at 930ºC and 0.1 MPa, so that there was no accumulation of char in the bed. However, the bituminous coals had much less reactive chars, so that there was a steady accumulation of char in the bed over the repeated cycles. More work is therefore needed to determine the suitability of the process for processing bituminous coals, as opposed to lignites. The high temperature used meant that Cu_2O was the oxidised form of copper during the reactions. The carrier was durable, no agglomeration occurred, and sulphur in the fuels did not appear to affect reactivity in these tests of up to eight cycles (Dennis and others, 2010).

In Germany, at the University of Siegen, as at a number of other locations, ilmenite is being investigated for use as an oxygen carrier for solid fuels because of its advantages of low toxicity and low cost (Schwebel and others, 2009). In this case, the plant arrangement envisaged uses a gravitating bed reducer (fuel reactor) and a fluidised bed oxidiser. The arrangement is based on the Herhof-IPV-Verfahren® waste and biomass gasifier. Advantages claimed include easier achievement of full fuel conversion, less need for char recovery from the fuel reactor outflow of carrier, adjustable residence time and reduced power demand. Experience in the area of biomass utilisation indicates an appropriate scale for the system of up to 20 MWth, while a capacity of up to 100 MWth could fit with minerals preparation (Schwebel and others, 2010; Schwebel, 2010). Initial tests in a 53 mm ID fixed bed reactor are being conducted using gaseous fuels and were described in Section 3.1.

At CSIC, Zaragoza, Spain, ilmenite has been tested as an oxygen carrier for CLC of a South African coal char using the 55 mm ID fluidised bed batch reactor referred to in Section 3.1 in connection with syngas CLC testing. The work involved successive oxidation-reduction cycles. Two batches of 2 g of coal char were introduced during each reduction period, and steam was used as fluidising/gasification agent. The 500 g charge of ilmenite was initially heated in air to 950ºC for 24 hours to oxidise it, and the cycles of reduction and oxidation were carried out at 900ºC. There was an increase in CO_2 production and reduction in H_2 and CO production as the cycles progressed owing to a gradual gain in ilmenite reactivity. Repeating the experiments using CO_2/steam mixtures as fluidising agent showed that significantly lower char conversion rates were obtained at high percentages of CO_2. For 100% steam, most of the char was gasified and the gaseous products had reacted within 15 minutes, whereas, for 100% CO_2, only 40% of the char had reacted after 30 minutes. However, as steam production uses energy, it may still be worthwhile recirculating part of the CO_2 (Cuadrat and others, 2010).

3.2.1 Chemical looping with oxygen uncoupling – CLOU

The Swedish team at Chalmers University have shown that chemical looping with oxygen uncoupling (CLOU), in which the oxygen carrier and conditions are selected to ensure that molecular oxygen is first released in the fuel reactor, could give more rapid reaction with solid fuels than conventional CLC. This is generally believed to be because the rate-determining char gasification process is avoided. CLOU could thus allow a smaller system with a smaller oxygen carrier inventory to be used, so reducing costs.

A CLOU oxygen carrier releases O_2 if the partial pressure of oxygen around the particles is lower than the equilibrium

Table 10 Conversion times for chemical looping with oxygen uncoupling (CLOU) and for CLC, using various fuels – tests at Chalmers University, Sweden (Leion and others, 2009a)

Time for 95% conversion, s	Mexican petroleum coke	South African coal	Indonesian coal	Colombian coal	German lignite	Swedish wood char
CLOU	41	40	30	51	25	28
CLC	648	612	282	606	84	378

partial pressure of oxygen for that material (Leion and others, 2009d). The latter can be determined from thermodynamic data. Three metal oxide systems identified as having potential to act as CLOU oxygen carriers because they have suitable equilibrium partial pressures of oxygen at temperatures relevant to combustion (800–1200ºC) are Mn_2O_3/Mn_3O_4, CuO/Cu_2O and Co_3O_4/CoO (Mattisson and others, 2009a). The Co_3O_4/CoO system is less well suited than the other two because it gives rise to a net heat input requirement in the fuel reactor. The latter would necessitate higher carrier recirculation rates to transfer sufficient heat from air reactor to fuel reactor (Leion and others, 2009d). Initial proof-of-concept of the CLOU system using CuO/Cu_2O and petroleum coke is described by Mattisson and others (2009a).

For the CuO/Cu_2O system, the oxygen is released while the copper is converted to a lower oxidation state, but not so far as to produce the element:

$$4CuO \leftrightarrow 2Cu_2O + O_2(g)\Delta H_{850} = 263.2 \text{ kJ/mol } O_2$$

In the air reactor in a CLOU system, the reduced metal oxide must be able to take the oxygen concentration sufficiently low that the excess air level is acceptable (4–5% by volume). Leion and others (2008b) showed that it was possible to re-oxidise the CuO/Cu_2O carrier at very close to the thermodynamic equilibrium partial pressure of oxygen. The latter corresponds to 1.5% and 4.5% of oxygen by volume at 900ºC and 950ºC respectively, and so this temperature range should be appropriate for the air reactor. In addition, since the reactions are exothermic in both reactors it should be possible to design a CLOU system such that the temperature is higher in the fuel reactor than in the air reactor. The lower air reactor temperature would facilitate the oxidation of the carrier and the higher temperature in the fuel reactor would make it possible to have a higher partial pressure or faster release of O_2 in the fuel reactor, increasing the fuel conversion rate (Leion and others, 2009a, 2010; Leion, 2010).

The system has now been tested with six fuels: three hard coals, a lignite, a petroleum coke and wood char (Leion and others, 2009a). Freeze granulation was used to prepare a 40% CuO carrier on ZrO_2 support, of final size 90–125 µm, spherical. 15 g samples, plus 15 g quartz sand, were placed in the small batch fluidised bed reactor described earlier in this section for tests of conventional CLC of solid fuels – *see* Figure 8 page 16. The carrier was first oxidised in 10% O_2 in N_2, then 0.1 g samples of several different crushed solid fuels (180–250 µm) added and nitrogen used as fluidising medium during the ensuing carrier reduction and fuel reaction period. 3–5 oxidation/reduction cycles were carried out in this way, and the off-gases analysed. The bed temperature was set to 950ºC at the beginning of each reduction step. The times for reaction of the various fuels are shown in Table 10, alongside those found for conventional CLC using the iron-based carrier ilmenite, at 970ºC in the presence of steam. The CLOU conversion, at 25–51 s for 95% conversion, was clearly substantially faster than CLC (three times faster for a lignite and up to fifteen times faster for some coals), despite the lower temperature and less reactive atmosphere used in the CLOU tests. It was also stated that it should be possible to achieve a complete conversion of carbon to CO_2 in a commercial CLOU unit (Leion and others, 2009a). Similar results were obtained in later experiments in the same apparatus, and the size of the fuel was not observed to have any significant effect on the fuel conversion rate, for particle sizes between 90 µm and 250 µm (Leion and others, 2010).

The Swedish researchers are also investigating $CaMn_{0.875}Ti_{0.125}O_3$ as a CLOU oxygen carrier (Leion and others, 2009d). This carrier was developed by SINTEF in Norway. $CaMnO_3$ itself is a potential oxygen carrier, but it has a tendency to decompose in an undesirable side reaction; however, incorporation of titanium stabilises it. TGA experiments were used to study formulations of slightly differing Ti content to determine the optimum formulation (shown above) and sintering temperature (1200–1250ºC). Reactivity decreases and attrition resistance increases with increasing sintering temperature. The main tests were performed on the optimised carrier using the batch fluidised bed apparatus described in the accounts of the CLOU experiments using CuO and in the accounts of the conventional CLC tests earlier in this chapter (*see* Figure 8). Methane and petroleum coke were the fuels used.

The methane tests over 30 reducing cycles showed no sign of decreased carrier reactivity. With petroleum coke fuel, higher temperature increased the conversion rate (*see* Table 11). The rate of conversion of petroleum coke was lower than with the Cu-based carrier because the release of oxygen from the particles was not as fast. However, compared with regular

Table 11 Conversion times and rates for chemical looping with oxygen uncoupling (CLOU) of petroleum coke – tests at Chalmers University, Sweden (Leion and others, 2009d)

	Time, min	Rate, min^{-1}
95% conversion, 900ºC	7.5	12.8
80% conversion, 900ºC	4.2	19.3
95% conversion, 950ºC	4.5	21.4
80% conversion, 950ºC	2.7	29.6

CLC at the same temperature, conversion of the fuel was more rapid. As for previous CLOU results, all the solid fuel was fully converted to CO_2, except for minor amounts likely to stem from an initial release of volatiles. Also as with Cu-based CLOU, the overall reactions in both the fuel and air reactor were exothermic, and so would reduce the required particle circulation rate in an actual system. Selection of temperature appeared less critical than for Cu-based CLOU. Overall, $CaMn_{0.875}Ti_{0.125}O_3$ was judged to be promising as a CLOU carrier (Leion and others, 2009d).

There is considerable ongoing work on other CLOU carriers based on more than one active metal because of their wider applicable temperature range and, particularly, lower cost than CuO/Cu_2O. Testing has been done using methane as well as solid fuels (Leion, 2010; Shulman and others, 2009; Azimi and others, 2010). The utility Vattenfall, which has close links with Chalmers University, views CLOU technology as the most promising way forward for commercial implementation of CLC (Strömberg, 2010).

Laboratory work on the decomposition of CuO to Cu_2O is being conducted at the University of Utah, USA to determine kinetic data and optimum conditions to aid reactor design (Eyring and others, 2010). Note also that evidence has emerged in recent work at the NETL, Morgantown, USA, that a carbon-containing fuel may actually facilitate the release of the oxygen by the carrier (Siriwardane and others, 2010a,b). The latter was described earlier in this section.

At Tsinghua University, Beijing, China, themogravimetric tests and small (30 mm ID) fluidised bed batch tests as well as modelling of the Co_3O_4/CoO system showed that this carrier was effective in the temperature range 685–860ºC, displaying high oxygen capacity, reaction rate and stability. Introduction of petroleum coke indicated that complete combustion was possible and that the reaction rate was limited only by the oxygen release rate (Li and others, 2009b).

3.3 Comments

The accounts in this chapter indicate that:

- methane can be combusted in CLC relatively easily, using manufactured carriers, such as spray-dried formulations incorporating nickel oxide;
- syngas, from coal gasification, should also be combustible in CLC using nickel-based manufactured carriers, but desulphurisation will be necessary to avoid deactivation and SO_2 release in the air reactor. Iron-based carriers are also effective;
- solid fuels, such as petroleum cokes or coals, can be combusted in CLC, but this will best be done using low-cost oxygen carriers because a greater quantity of carrier replenishment will be needed than for the more easily pre-cleaned gaseous fuels. Iron-based materials such as oxide scale or ilmenite appear to be suitable and also insensitive to impurities. Chemical looping with oxygen uncoupling (CLOU) offers a way to achieve much greater reaction rates that could reduce the overall cost of CLC.

4 PDU tests

4.1 PDUs for gaseous fuels

In a workable CLC system, it is essential to maintain intimate contact between the solid carrier and the reacting fuel in the fuel reactor, and between the carrier and air in the air reactor (Hossain and de Lasa, 2008). In the interconnected fluidised bed systems most commonly suggested for achieving this (*see* Figure 13), the fuel reactor is a bubbling fluidised bed and the air reactor is a fast fluidised bed. The latter assists solids recirculation around the system and accommodates the higher volumetric gas flow on the air side (Lyngfelt and others, 2001). Gas sealing between the reactors is achieved by using loop seals. Operating the air reactor hotter than the fuel reactor allows the external recycling of regenerated oxygen carrier to transfer heat from the air reactor to the fuel reactor if necessary, if the fuel reaction is endothermic or not sufficiently exothermic. Variations of the basic concept exist. For example, in attempts to maximise oxidation of the carrier, workers in Canada have modified it to incorporate recycling of a portion of the solids captured by the primary cyclone to the base of the air reactor in addition to the normal return of the solids to the fuel reactor (Xu and others, 2009a,b; Cheung and others, 2010).

In the joint ECSC-funded project conducted in Sweden, Spain and Austria, referred to in Section 3.1, mathematical and cold flow fluidised bed models were used to develop and optimise reactor designs for both atmospheric pressure and pressurised systems for syngas combustion. Pressurised systems could form the basis of coal CLC systems involving combined cycles. One of the cold models was used as the basis for the design of a 300 Wth continuously operating atmospheric pressure process development unit at Chalmers University, Sweden, which is now used for screening carrier performance, agglomeration and attrition characteristics and to determine kinetics for comparison with theoretical calculations. This system allows smaller samples of candidate carriers to be used than are required for testing in the larger PDUs described later in this section. As an example, the smaller system was used to test carriers based on Ni, Mn and Fe. In tests on simulated syngas (50% CO, 50% H_2), 60% Fe_2O_3 with Al_2O_3, 60% NiO with $MgAl_2O_4$, and 40% Mn_3O_4 with ZrO_2 doped with Mg, all prepared using freeze granulation, were used (Mattisson and others, 2007). The freeze granulation procedure was described earlier by Cho and others (2004). Tests have also been conducted on the combustion of natural gas in this apparatus using NiO with $MgAl_2O_4$ carrier (*see, for example,* Johansson and others, 2006).

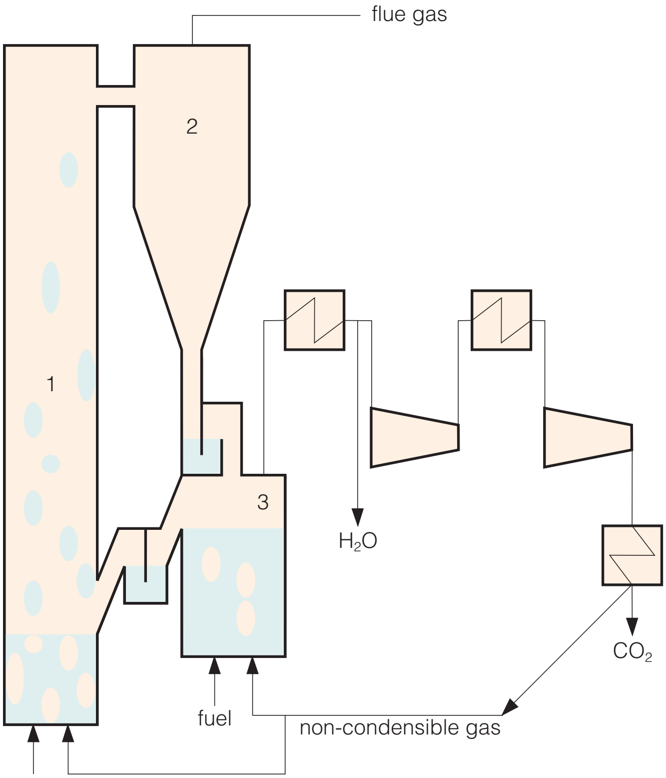


Figure 13 Chemical looping combustion process using two interconnected fluidised beds (Lyngfelt and others, 2001)

The tests confirmed the suitability of the three carriers referred to above for converting syngas, all giving a high fuel conversion (around 99% or higher). With the Ni-based carrier, the fraction of CO and H_2 remaining in the product gases was in the range 0.01–2.3%. Reaction was complete and no CO or H_2 remained when the Mn-based carrier was used. The carriers were recirculated in hot conditions (800–950ºC) for 150 h (Ni), 130 h (Mn) and 60 h (Fe) without deactivation or agglomeration and very little attrition. Losses were also very small (0– 0.039%/h). The iron and manganese-based carriers are particularly interesting for these applications, as they are considerably less expensive than nickel-based carriers (Mattisson and others, 2006, 2007).

Under the EU *CO_2 Capture Project* and the project *Chemical Looping Combustion – CLC Gas Power*, NiO-based carriers on different forms of alumina were tested for methane combustion in a 500 Wth continuous CLC system at CSIC, Zaragoza, Spain (Adánez and others, 2009b). Initial screening tests in TGA and batch fluidised bed apparatus revealed that NiO carriers impregnated on α-Al_2O_3, $MgAl_2O_4$ or $CaAl_2O_4$ had a high content of free NiO and high selectivity toward CO_2 and H_2O. Some tests used H_2S addition, to examine its effects, as discussed in Chapter 7. The 500 Wth continuous PDU is also described in that section and shown in Figure 30. 175 h of operational experience was gained. No agglomeration or carbon deposition occurred and the maximum combustion efficiency achieved was 99% at an oxygen carrier:fuel ratio of 3:1 x stoichiometric, but H_2 and CO were formed (increasingly at lower solids circulation rates) together with the CO_2.

A 10 kWth prototype PDU based on linked fluidised beds (bubbling bed for fuel reactor, fast bed with riser for air reactor) was developed at Instituto de Carboquímica (CSIC), Zaragoza, Spain, and used to examine the performance of a

CuO/Al_2O_3 carrier, prepared by dry impregnation, in combusting methane (Adánez and others, 2006). These showed that, at a fuel reactor temperature of 800°C, a carrier to fuel (methane) ratio of 1.4 times stoichiometric was needed to achieve complete combustion. Using the stoichiometric quantity gave around 90% combustion. Agglomeration (a potential issue for copper-based carriers) was not found to be a problem. Attrition, initially high, decreased rapidly to a low value, and carrier reduction reactivity was maintained.

A mathematical model of the fuel reactor (fluid dynamics and chemical reactions) was also validated against the data obtained from the 10 kWth PDU. The model predicted adequately the results obtained, for example that, in general, an oxygen carrier-to-fuel ratio of 1:4 (x stoichiometric) was needed to fully convert methane at 800ºC. A minimum solids inventory of 75 kg per MWth was needed to reach a predicted combustion efficiency of 99.9% for an oxygen carrier to fuel ratio >2 at 1073K (Abad and others, 2009).

10 kWth PDUs, which use interconnected fluidised beds (bubbling for fuel reactor, fast for air reactor with riser), are used at Chalmers University of Technology, for gaseous and solid fuels (*see, for example*, Lyngfelt and others, 2008; Berguerand and Lyngfelt, 2008a,b; Berguerand and others, 2010). Tests of NiO-based carriers in the gaseous fuels CLC system were carried out for over 1000 h on methane, under the *CO_2 Capture Project* and the project *Chemical Looping Combustion – CLC Gas Power*. These carriers were prepared by spray drying. These successful tests showed that it is possible to produce a good oxygen carrier from commercial raw materials using spray drying and that long-term operation, with very little carrier particle loss, on natural gas is feasible (Linderholm and others, 2009).

At the Korea Institute of Energy Research, Daejeon, a 50 kWth continuous CLC PDU of novel design has been operated on natural gas and synthesis gas (containing by volume 43.3% CO, 39.4% H_2) fuels at steady state for over 50 h, using NiO/bentonite and $Co_xO_y/CoAl_2O_4$ (20 kg + 40 kg) oxygen carriers (Ryu and others, 2009b, 2010a). The nickel-based carrier was prepared by physical mixing and the cobalt-based carrier was prepared by co-precipitation and impregnation. The PDU is shown in Figure 14. It has two bubbling fluidised beds without loopseals. Instead, a solid injection nozzle and a downcomer are located inside each reactor to circulate oxygen carrier particles. The cyclone above each reactor separates the oxygen carrier from the gas stream then send the material via the downcomer to the other vessel. Steady temperatures (~900ºC and 800–900ºC on natural gas and syngas, respectively) were maintained throughout the operations. Pressure drops in the two reactors were also stable, and indicated that the solids recirculation around the system was smooth and stable.

There was insignificant or zero production of NOx by the oxidation reactor on both natural gas and syngas. There was also no CO_2 or CO detected in the oxidiser outlet stream, showing that no carbon was transferred from reducer to oxidiser. In the reducer, high fuel conversion and CO_2 selectivity were achieved and CO, CH_4, and H_2 concentrations were maintained at very low levels. Only 0.6% CO remained in the reducer product gas from syngas combustion. The balance of the product gases was almost entirely CO_2 (99.4%) (Ryu and others, 2009b, 2010a), although TGA tests showed that higher CO_2 concentrations in the reduction reactor can reduce the reactivity of oxygen carriers (Ryu and others, 2010b). Staged fuel (methane) introduction was therefore

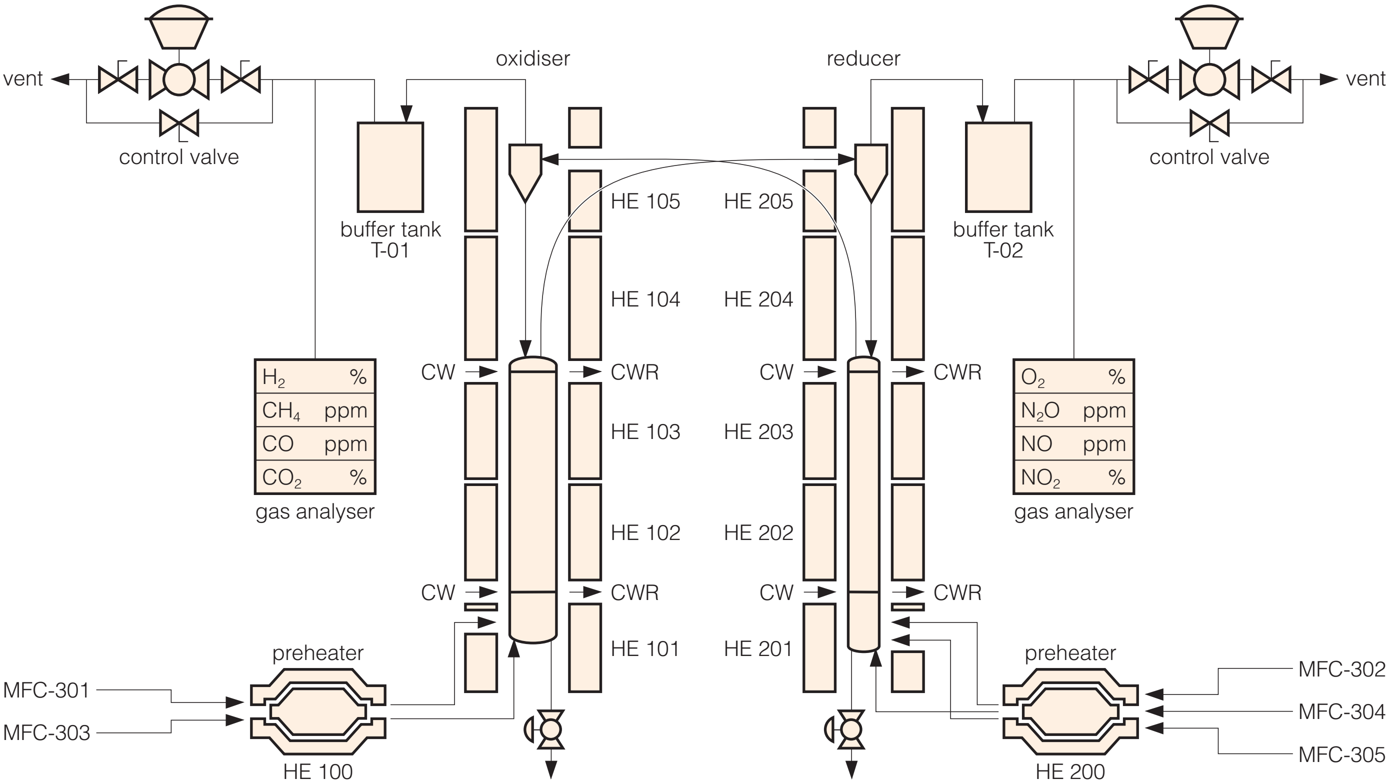


Figure 14 50 kWth continuous CLC PDU at the Korea Institute of Energy Research, Daejeon (Ryu and others, 2010a) tested in the 50 kWth CLC fuel reactor and shown partially to offset this. A 3 kWth CLC system is currently being characterised in cold flow tests (Ryu and others, 2010c).

In Austria, at the Vienna University of Technology, there is the largest currently operating CLC. This is a 120 kWth dual circulating fluidised bed (DCFB) system for CLC of gaseous fuels including syngas. There is also a cold model for studying its fluid dynamics (Kolbitsch and others, 2008, 2009; Pröll and others, 2008). The main difference in the fuel reactor from most other systems is that it is operated at close to turbulent conditions, in order to improve gas-solid contact and so avoid fuel slip. Both air reactor and fuel reactor are designed as circulating beds (*see* Figure 15). The cold tests have shown that a high overall solids circulation is achievable with the system, and that the global solids circulation can be effectively controlled by staged introduction of fluidisation medium in the air reactor. Hence, the fuel reactor can be optimised for fuel conversion without attention to oxygen carrier circulation (Kolbitsch and others, 2009).

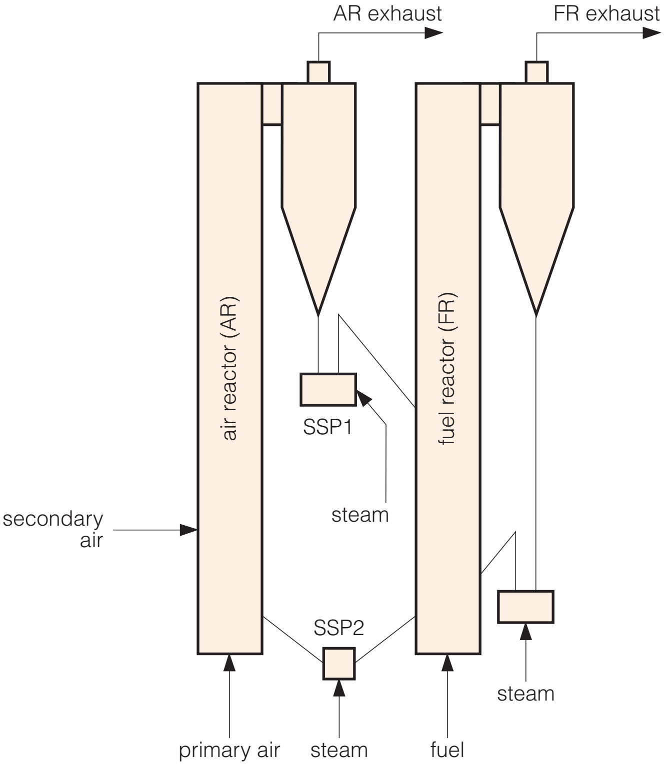


Figure 15 120 kWth dual circulating fluidised bed (DCFB) CLC system at Vienna University of Technology (Kolbitsch and others, 2009)

The hot rig itself was designed for high solids circulation, low solids inventories and low solids residence times, and to give results relevant to future scaled-up plants, although residence times are partly restricted by the size of the apparatus that can be accommodated (Bolhàr-Nordenkampf and others, 2009; Kolbitsch and others, 2009). Very high solids circulation is needed at full load and, due to the low solids inventory in the reactors, the solids residence time was very short. The active solids in the reactors constituted less than 50% of the total inventory, but this proportion should increase with plant size (Kolbitsch and others, 2009).

In this plant, Ni-based carriers have achieved high CH_4 conversion and high CO_2 yields. It was found that fuel conversion passed through a maximum (of 96% and 99% for two different Ni-based carriers) at a temperature of about 900ºC. The CO_2 yield increased throughout the temperature range of 800–950ºC (reaching around 90% and 94% for the two different carriers) and with increasing air/fuel ratio (Bolhàr-Nordenkampf and others, 2009). The tests with the design Ni-based carrier used three fuels: hydrogen, CO and CH_4, and these were successfully introduced at rates of 65–145 kW (Kolbitsch and others, 2009). With methane, CH_4 conversion and CO_2 yield increased with fuel power input at a constant global air:fuel ratio and temperature, even though this implied a decrease in specific solids inventory (Pröll and others, 2009b). In separately reported trials, carried out at a fixed fuel reactor temperature of 900ºC, similar results were obtained, and the increase in CH_4 conversion and CO_2 yield with increasing fuel power was also confirmed, and attributed to the gas-solids contacting improving at increasing gas velocities, within the range tested, despite a shorter residence time. 10–20 MWth was suggested as the most appropriate next scale using NiO carriers, at which niche applications in steam generation or natural gas reforming could fit (Pröll and others, 2010).

This plant was designed to test Ni-based oxygen carriers, but tests have also been performed using much less expensive natural materials (ilmenite – of mean diameter >200 µm – and ilmenite with added olivine, the latter for methane combustion) for gaseous fuels (Kolbitsch and others, 2009;

Table 12 Operating parameters for continuous CLC tests using ilmenite in 120 MWth DCFB system at Vienna University of Technology (Pröll and others, 2009a)

Parameter	Fuel		
	$H_2 + N_2$	H_2 + CO	Natural gas
Fuel power, kW	24–43	40–92	20–130
Temperature, air reactor, ºC	895–978	887–983	813–986
Temperature, fuel reactor, ºC	894–966	878–976	839–969
Content of O_2 in air reactor exhaust, % vol, dry	8.5–11.0	9.3–14.2	3.6–12.8
Total mass of ilmenite, kg	70–90	70–85	70–90
Total mass of additive (olivine), kg	0	0	0–15

Pröll and others, 2009a). 90–95% conversion of hydrogen was achieved even in initial, non-optimised, tests with ilmenite. Operating conditions on hydrogen+nitrogen (up to 43 kW), CO+H_2 mixtures (up to 92 kW) and methane (up to 130 kW) are shown in Table 12. Defluidisation was at first encountered, but this was solved by oxidative pre-treatment of the ilmenite for 3–6 h at 850ºC. Run times were 12–16 h. In these tests, the upper regions of the fuel reactor were very lean in solids and no real circulating regime was reached in this reactor because of the need for lower gas velocities due to limited fuel conversion and use of oversize solids. However, the system design conditions are for a mean carrier particle diameter of only 120 µm, to permit full fuel conversion (Pröll and others, 2009a). Figure 16 shows the performance (fuel conversion versus fuel input power) on a 1:1 H_2:CO fuel mixture (Pröll and others, 2009a). A slight decrease of fuel conversion occurred with increasing load, related to gas-solids contact time decreasing in the fuel reactor, but the non-optimal fluid dynamic situation in the fuel reactor for the reasons referred to above indicates that an improvement of syngas conversion is likely to be achievable in the future. This should also be relevant to CLC of solid fuels. However, there are not any current plans to use coal. The latter would require a redesign of the fuel reactor (Mayer, 2010).

The performance of NiO-based oxygen carriers in combination with ilmenite was close to that of the NiO-based carriers up to a proportion of ilmenite of up to 90% by wt. Consequently, dilution of highly active oxygen carriers with ilmenite could improve the economics of methane-fuelled CLC systems (Mayer and others, 2010).

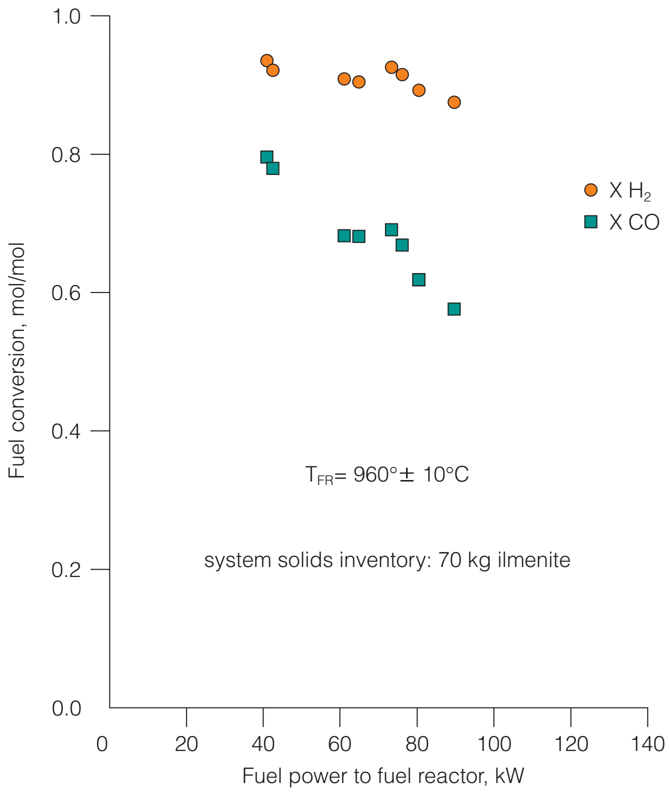


Figure 16 Fuel conversion for CLC of simulated syngas (Pröll and others, 2009a)

4.2 PDUs for solid fuels

For direct CLC of solid fuels, there are other issues, because there is a sequence of reactions to occur in achieving complete conversion to CO_2. Small-scale batch tests on CLC of coals at Chalmers University, Sweden, were described in Section 3.2. These were followed by continuous tests under the ENCAP project with a South African coal (analysis in Table 13) in a purpose-built 10 kWth continuous CLC system based on the gaseous CLC pilot plant at Chalmers (Berguerand and Lyngfelt, 2008b). Ilmenite (90–250 µm) was used as carrier. Modifications to the design were made in the area of the fuel reactor and an additional solids recirculation loop was incorporated. The fuel reactor design is shown in Figure 17. It has three chambers:

1 a low velocity part, where the fuel particles devolatilise, are gasified and the volatiles and the syngas reduce the

Table 13 Analysis of South African coal used in batch and continuous chemical looping tests at Chalmers University, Sweden (Berguerand and Lyngfelt, 2008b, 2010)

C %, wt%	62.5
H %, wt%	3.5
N %, wt%	1.4
S %, wt%	0.7
O %, wt%	7.7
Volatile matter %, wt%	21.6
Moisture, % ar	8.3
Ash %, w/w	15.9
LHV, MJ/kg	23.9

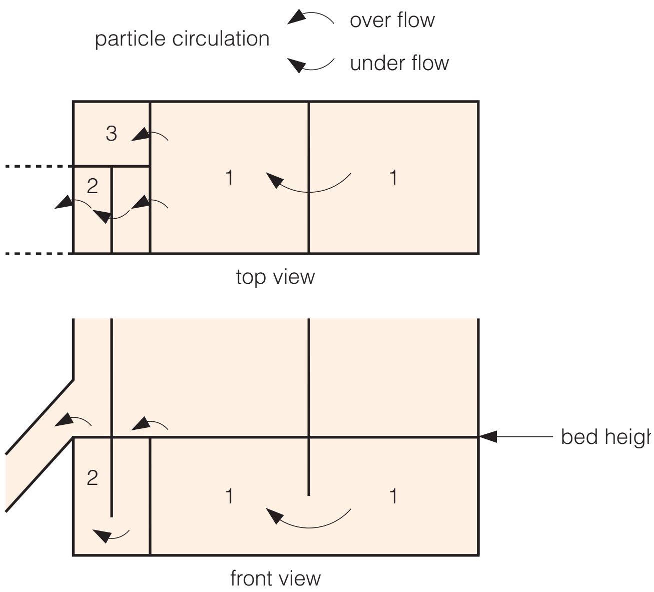


Figure 17 Fuel reactor configuration of 10 kWth solid fuels CLC at Chalmers University (Berguerand and Lyngfelt, 2008b)

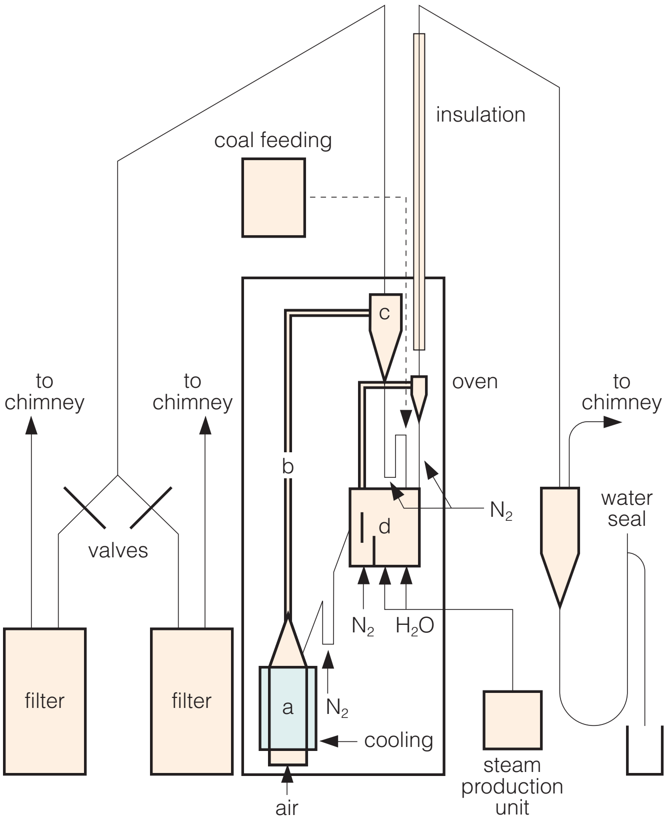


Figure 18 10 kWth solid fuels CLC system at Chalmers University (Berguerand and Lyngfelt, 2008b)

oxidised carrier. This chamber is itself divided by a wall with an opening at the bottom, through which the particles are forced to pass;

2. a carbon stripper for separating carbonaceous particles from the metal oxides; the former are recovered from its leaving gas flow by a small cyclone; the metal oxide particles continue to the air reactor via a lower particle lock (loop seal);
3. a high velocity part, where a proportion of both particle types is entrained, in order to provide recirculation and recycle to the fuel reactor, via the small fuel reactor cyclone.

The whole system is shown in Figure 18. In the fuel reactor, the gasifying/fluidising gas of the low velocity section is steam. Nitrogen is usually used in the carbon stripper and the high velocity part, although steam can be substituted. Loop seals are fluidised with nitrogen normally. There was apparently no system for ash removal from the equipment for these relatively short (up to 2 h duration) proof of concept tests. Some basic operating parameters of the plant are shown in Table 14.

Fourteen tests were performed with the South African coal with a total duration of fuel feed (at 0.5 kg/h) of 22 h over fourteen tests, with 12 h in total of stable operation. The paper tabulates averaged results for each of the tests and also describes in considerable detail the results from two of the more reliable tests (Berguerand and Lyngfelt, 2008b). Some of the averaged results are shown in Table 15. Although steady state was believed to be achieved, this was not generally shown in the mass balances, which were believed to be affected by nitrogen leaks leading to an overestimation of the carbon flows from the fuel reactor.

These first continuous tests showed that, overall, the use of solid fuel in a continuous CLC system was feasible, but conversion of fuel was only 50–80%. This was due to the small size of the fuel reactor cyclone, which resulted in a poor separation of fine material compared with a commercial-sized cyclone. The researchers estimated that a fuel conversion perhaps as high as 98–99% should be possible in a larger system with well-optimised cyclones. CO_2 capture was in the range 82–96%, which was as expected from the laboratory tests, but it was also expected that a well-optimised full-scale carbon stripper would increase this. The conversion of the char gasification products indicated a possible need for an oxygen polishing step, as previously indicated by the small batch tests. However, the degree of gaseous conversion to CO_2 should be much better in still larger systems, where there would be better mixing and greater residence times. The ilmenite carrier performed well, with little attrition, agglomeration or loss of activity (Berguerand and Lyngfelt, 2008b).

With a Mexican petroleum coke as fuel (*see* Table 16), again using ilmenite as oxygen carrier, stable operation was demonstrated for a total of 11 h (over two tests), but the CO_2 capture efficiency was only 60–75%. This was attributed to the low reactivity of this fuel. The solid fuel conversion was 66–78% even with an improved fuel reactor recycle cyclone, but this was still penalised by the small cyclone's low efficiency. Attrition of the ilmenite oxygen carrier was low: losses, estimated at 0.01–0.03%/h, were considered promising for such a low-cost material (Berguerand and Lyngfelt, 2008a).

Key issues identified or confirmed by the Swedish team from these first continuous tests on the solid fuels were:

- char gasification is slow (although faster than in conventional gasifiers), so a long residence time and a high capture efficiency for the cyclone above the fuel reactor are needed to achieve a high degree of conversion;
- good gas/solids contacting is essential so that the reducing gases produced by volatiles release and char

Table 14 Basic operating parameters of 10 kWth continuous solids CLC system at Chalmers University, Sweden (Berguerand and Lyngfelt, 2008b)

Carrier particle size range, µm	Average carrier size, µm	Average coal particle size, µm	Air reactor operating temperature, ºC	Fuel reactor operating temperature, ºC	Solids inventory, kg/MWth
100–200	150	250	1000	950	500

Table 15 CLC tests on South African coal in 10 kW continuous PDU at Chalmers University, Sweden (Berguerand and Lyngfelt, 2008b)

Test number	Feed duration/ accumulated time, min	Stable time, min	CO_2 fraction in total carbon leaving FR, %	Fuel conversion, %	Fuel power, kWth
1	20	0	–	–	–
2	71/91	20	–	–	–
3	130/221	82	80	66	2.2
4	161/382	50	80.5	79	2.6
5	110/492	0	–	–	–
6	43/535	15	–	–	–
7	92/627	45	80	78	2.6
8	55/682	45	78	58	1.9
9	84/766	70	77	50	1.7
10	145/911	80	81	73	2.4
11	143/1054	95	78	53	1.75
12	79/1133	60	80	80	2.7
13	125/1258	0	–	–	–
14	70/1328	8	85	–	–

Table 16 Analysis of Mexican petroleum coke used in continuous chemical looping tests at Chalmers University, Sweden (Berguerand and Lyngfelt, 2008a)

C%, ar	81.32
H %, ar	2.87
N %, ar	0.88
S %, ar	6.02
O %, ar	0.45
H_2O %, ar	8.0
Ash %, ar	0.46
Heating value, MJ/kg	31.75

gasification react with the oxygen-carrier. Complete oxidation may not be possible in practice, in which case downstream measures, for example oxygen injection at the fuel reactor outlet, may be needed;

- CO_2 capture will be incomplete if there is loss of unconverted char to the air reactor. Sufficient residence time in the fuel reactor is needed to minimise this, but char still remaining in this stream can be stripped off in a carbon stripper;
- good contact is needed between the oxygen carrier and the reducing gases released from the fuel particles to minimise inefficiencies through unconverted gases such as CO and H_2 leaving the fuel reactor.

The same 10 kW unit was subsequently operated using batch feeding of petroleum coke and of the South African coal to enable the influence of parameters such as particle circulation and fuel reactor temperature to be further studied (Berguerand and Lyngfelt, 2010). Tests were conducted both with and without particle recirculation between the reactors. 25 g batches of fuel were introduced in clingfilm bags. Again, ilmenite was the carrier. The mass of carrier in the low velocity section of the fuel reactor was approximately 5 kg. Increasing the temperature in the fuel reactor increased the rate of reaction markedly, linked to the temperature dependence of fuel gasification. For petroleum coke, it increased from an average of 17.4%/min at 950°C to 40%/min at 1030°C. For the South African coal, it increased from 47%/min at 970°C to 101%/min at 1000°C. There was general agreement between the results of the batch feed tests and tests using continuous feeding, indicating the validity of the method used for batch feeding (in bags) to acquire data.

It was suggested that high temperatures should be used to reduce the need for long residence times in the fuel reactor. The tests with particle recirculation showed that 75% of the total oxygen demand in the fuel reactor was associated with the volatiles, if sulphur is included. This was despite the fact that the two fuels tested had low volatile matter contents. It was concluded that this very high proportion expended on the volatiles was more a consequence of reactor design and the fuel feeding method (dropped onto the fluidised bed) than a problem inherent to the CLC process. It should be possible to avoid the problem of high oxygen demand in a commercial system by introducing the fuel at the base of the fluidised bed. In addition, to achieve maximum CO_2 purity, it may be necessary to use downstream oxygen injection, sequential fuel reactors, or other measures (Berguerand and Lyngfelt, 2010; Berguerand and others, 2010).

In China, at Southeast University in Nanjing, Shen and others (2009a,b) used a spouted, rather than a bubbling, fluidised bed for the (~10 kWth) fuel reactor, introducing the coal with CO_2 and some steam as fluidising medium at the base of the bed (*see* Figure 19). In this case, a nickel oxide-based carrier was selected, despite its high cost rendering it unlikely to be used in commercial systems fuelled directly by coal. Recycled flue gas would provide the fluidising medium in a larger CLC unit. A spouted bed has a locally higher fluidising velocity just above the point of introduction of the fluidising medium, and this arrangement can provide stronger mixing and more rapid heating of the introduced coal, potentially enabling coal conversion to CO_2 to be increased, as well as discouraging agglomeration. The spouted bed vessel was rectangular, internal dimensions 230 mm x 40 mm, with a 60° conical base. The air reactor was the usual high velocity fluidised bed.

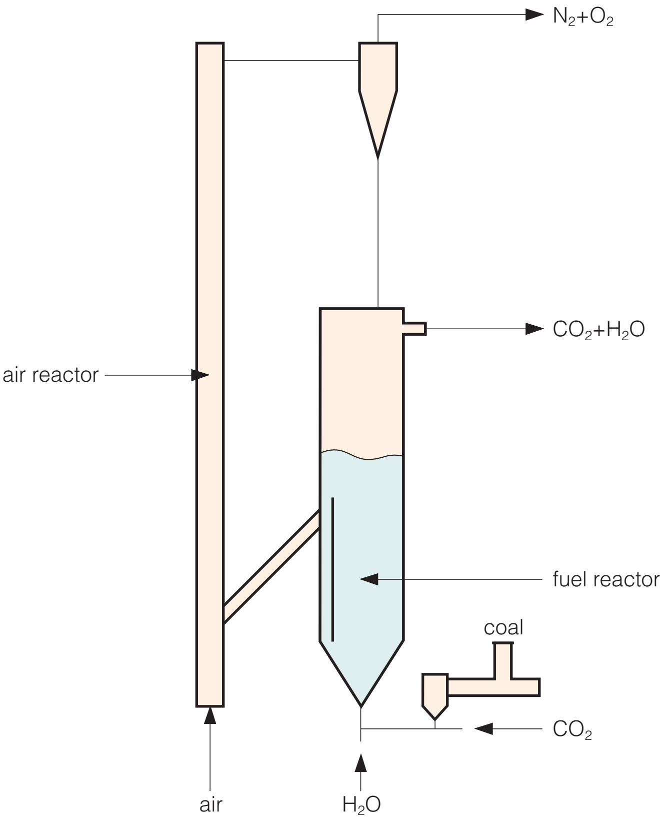


Figure 19 10 kWth CLC with spouted fluidised bed fuel reactor at Southeast University, Nanjing, China (Shen and others, 2009b)

Table 17 Analyses of Shenhua coal used in continuous CLC tests in 10 kWth PDU at Southeast University, Nanjing (Shen and others, 2009a,b)

Proximate analysis, %, ar		Ultimate analysis, %, ar	
Moisture	6.98	C	65.06
Fixed carbon	53.85	H	4.34
Volatile matter	33.59	O	15.98
Ash	5.58	N	0.86
		S	1.2
LHV, MJ/kg	24.80		

In the first tests, the carrier consisted of 32.7% NiO and 67.3% $NiAl_2O_4$, prepared by impregnation, sintered at 1100ºC. $NiAl_2O_4$ has a high mechanical strength and good resistance to chemical attack. The fuel was Shenhua bituminous coal (analysis in Table 17). Gas analyses by GC were carried out on samples after steady operating conditions were achieved for a period of an hour. The coal feed rate was 1.2 kg/h (around 8 kWth). At higher temperatures the CO_2 proportion increased, reaching over 95% by volume at 960ºC. The return of spent oxygen carrier was accomplished using an overflow system incorporating a loop seal as part of the fuel reactor, as shown in Figure 19. The comparatively large cross-sectional area of this part of the reactor meant that CO_2 losses to the air reactor were larger than would be the case in a larger-scale CLC plant. Consequently, some CO_2 (about 5% by volume) was observed in the exit gas from the air reactor. Carbon utilisation varied with fuel reactor temperature. The maximum carbon conversion efficiency (92.8%) showed that not all the carbon exited the system as CO_2, CO or CH_4, but that some elutriation of fine char occurred. CO_2 capture efficiency reached 80%, at a fuel reactor temperature of 960ºC, but this should be improvable in larger equipment, in which CO_2 leakage from the fuel reactor to the air reactor would be proportionally less. The coal used had a low ash content (5.6%) and this was largely incidentally removed from the system through elutriation from the fuel reactor spouted fluidised bed so any effects from ash interactions with the carrier were not apparent during these comparatively short duration tests, which lasted for sixty minutes (Shen and others, 2009a).

Further tests were carried out in the same equipment to examine more closely trends in carrier reactivity over time. The 100 h experiments were divided into four stages, each characterised by a different operating temperature (*see* Table 18). In this case, the carrier was prepared by co-precipitation of 35% NiO and 65% Al_2O_3, followed by heating at 1000ºC. The calcination converts the alumina to $NiAl_2O_4$. The fuel was again Shenhua bituminous coal (*see* Table 17 for analysis). Samples of the carrier were removed at the end of each of the four stages of the test, for analyses by XRD, SEM and X-ray fluorescence. XRD showed the initial, calcined carrier consisted of only NiO and $NiAl_2O_4$. The CLC tests and subsequent analyses showed that the reactivity decreased markedly over the 100 h of testing and that this was due to mainly to sintering during oxidation in the air reactor. Sintering caused agglomeration, which reduced the BET-determined surface area and pore volume of the particles. It was concluded that control of external particle circulation between air reactor and fuel reactor will be important to reduce the temperature of the particles in the air reactor to minimise deactivation. The coal ash and sulphur made no significant contribution to the loss in reactivity. Admission of steam to the fuel reactor reduced the extent of deactivation (Shen and others, 2009b). The 10 kWth PDU is also being used to test the CLC of biomass (sawdust) using an iron oxide oxygen carrier (Shen and others, 2009c).

A smaller (1 kWth) PDU with a spouted bed fuel reactor at Southeast University has been used to investigate the effect of sulphur in the coal (Shenhua – *see* Table 19) on a nickel-based carrier (Shen and others, 2010). This is

Table 18 Operating parameters in the 10 kWth continuous CLC PDU with spouted bed fuel reactor at Southeast University, Nanjing (Shen and others, 2009b)

	Stage A	Stage B	Stage C	Stage D
Operating time, h	30	30	30	10
Fuel reactor temperature, ºC	920	940	960	980
Air reactor temperature, ºC	980–990	1000–1010	1030–1040	1050–1060

Table 19 Analyses of Shenhua coal used in continuous CLC tests in 1 kWth PDU at Southeast University, Nanjing (Shen and others, 2010)

Proximate analysis, %, ar		Ultimate analysis, %, db	
Moisture	8.7	C	74.62
Volatile matter	32.65	H	4.65
Ash	6.39	O	12.70
		N	1.02
		S	0.62

discussed in Section 8.1. Steam was used as fluidising agent and it was found that char conversion was greatly increased at higher temperatures.

CLC using iron ore carrier is also under investigation at Southeast University (Wu and others, 2010). Low-cost natural materials are more likely to be suited to use as oxygen carriers for combustion of coals, and the 1 kWth PDU was used to test the use of an iron ore (a haematite from Australia). This carrier (active constituent Fe_2O_3) was used in ten hours of operation at a fuel flow of 0.7 kW at a fuel reactor temperature of 950°C. Shenhua bituminous coal was again the fuel; the analysis of the samples for these tests was very close to that shown in Table 17. Steam was used as fluidising agent. The CO_2 capture efficiency obtained was about 85%. The conversion was 82–87%. Some CO_2 was released in the air reactor outlet stream, showing that some residual char was transported with the recirculating carrier to this reactor. There was some loss of carrier due to attrition (0.0625%/h). XRD analysis showed that after 10 h of operation, both Fe_2O_3 and Fe_3O_4 were present in the oxidised iron ore of the air reactor, and Fe_2O_3, Fe_3O_4, FeO and Fe_2SiO_4 in the reduced iron ore of the fuel reactor. The tests confirmed the suitability of the iron ore carrier for CLC of solid fuels (Wu and others, 2010). Chapter 7 describes a pressurised CLC combined cycle that it is proposed would use the spouted bed fuel combustor system with an iron oxide carrier. Carrier tests at pressure in a laboratory fixed bed reactor were reported in Section 3.2 (Song and others, 2010).

A 1 MWth test facility (*see* Figure 20) has been erected at the Technical University of Darmstadt, Germany, to test the technical feasibility of chemical-looping combustion of coal as well as the application of carbonate looping (Epple and Ströhle, 2008; Beal and others, 2010; Ströhle and others, 2010; Vattenfall, 2010). This is the main part of the EU RFCS-funded project ECLAIR (Emission Free Chemical Looping Coal Combustion Process), a four-year multi-partner programme involving also Chalmers University, CSIC, Sintef, Air Liquide, Vattenfall and Alstom. The air reactor of the 1 MWth plant is currently being commissioned (Epple, 2010). The oxygen carrier will primarily be ilmenite. Two testing phases are planned, including a components modification phase to optimise process efficiency. In the first tests, an ash-free char will be used; subsequent modifications will allow ash separation to be incorporated to enable coal feeding. The results from this and from a 100 kWth plant to be constructed at Chalmers will be used to identify technical issues and to provide data for a design study for a 450 MWe commercial unit. The latter will include estimating performance, including impact of using 700–720ºC steam temperatures, and emissions and other environmental impacts. However, the next stage in scale-up is expected to be to 10–50 MWe (Beal and others, 2010).

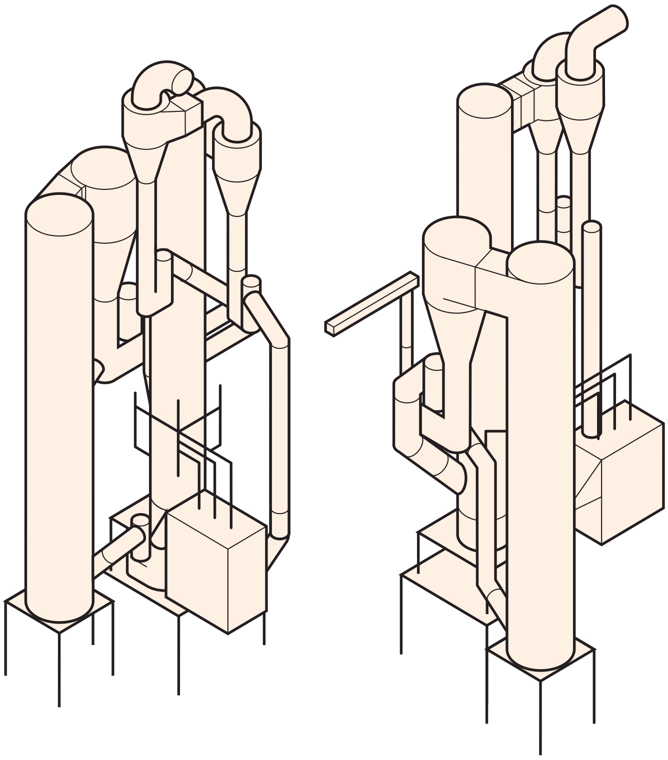


Figure 20 1 MWth CLC facility at the Technical University of Darmstadt, Germany (Beal and others, 2010)

4.3 Design aspects

In a practical system, the oxygen carrier inventory needs to be minimised to limit vessel sizes and costs and fluidisation energy requirements. The bed mass is inversely related to the carrier conversion rate, and the key concern is that increased bed mass results in greater power demand for fluidisation, reducing thermal efficiency. This is particularly the case for the oxidation reactor, where air flow rates are high. Estimates of the required combined bed mass for the reduction and oxidation reactor on methane fuel are 460–620 kg/MWth for CuO and NiO carriers supported on alumina (Mattisson and others, 2003) and, for the fuel reactor alone, 80–330 kg/MWth for Ni, Cu and Fe-based carriers on alumina (Cho and others, 2004). Workers at CSIC have used TGA test results to make approximate estimates of the required recirculation rate and solids inventory for a CLC using ilmenite to combust coal. The recirculation rate determines the size of the air reactor riser. Taking into account commercial experience in CFB systems, the maximum economically feasible recirculation rate for CLC was estimated to be 16 kg/s per MWth. The estimated inventory after initial stabilisation in activity was 350 kg/MWth in the fuel reactor (Adánez and others, 2010).

4.4 Comments

In a CLC system, it is necessary to maintain intimate contact between the solid carrier and the reacting fuel in the fuel reactor and with the carrier and air in the air reactor. To achieve this, there have been various designs proposed and tested in the form of small- and medium-sized process development units. Fluidised bed(s) are a feature of most of these, whether for combusting gaseous fuels or solid fuels. The air reactor is usually a fast fluidised bed with a riser. Experience in somewhat similar technology areas is substantial, such as in fluid catalytic cracking and CFBC. Different methods of gas sealing while allowing solids connection between the oxidiser and reducer have been used successfully. Most of these are variants of loop seals, fluidised with steam. Continuous tests using such systems on both gaseous and solid fuels have shown that the process concept can be successfully implemented, and the scale is gradually increasing. The scale of CLC has recently reached 1 MWth, in the form of the continuous pilot plant that will use solid fuels that has been constructed at the Technical University of Darmstadt, Germany. The results from this will feed into a design study for a 450 MWe commercial unit. However, the next stage in scale-up is expected to be to 10–50 MWe.

5 Other oxygen chemical looping systems

In some proposed chemical looping processes, the oxygen carrier would be used to supply oxygen for processing a solid fuel such as coal, within cycles producing hydrogen and CO_2. In these, the hydrogen is formed from reaction of steam with the recirculating carrier. These would be more complex cycles than conventional CLC and are probably further from application.

In Canada, at the University of Ontario Institute of Technology, Gnanapragasam and others (2009) in process simulations compared what they called coal direct chemical looping (CDCL) with a cycle using chemical looping for syngas combustion (SCL) following conventional gasification. Figure 21 shows the CDCL cycle. Both cycles are aimed at hydrogen production and CO_2 capture. Haematite is fed as oxygen carrier to the fuel reactor in CDCL and to the syngas combustor in the SCL system. In each case, the hydrogen is produced subsequently by reaction of the Fe/FeO mixture exiting the first stages with steam. The magnetite formed in hydrogen production is re-oxidised to Fe_2O_3 in an air reactor. The syngas chemical looping scheme uses two reaction vessels in series, separated by gas separation for each of the three parts of the process. The CDCL system is a slightly less complex cycle and has some advantage in having a reduced oxygen consumption (some is still fed to the fuel reactor for partial combustion) and producing more hydrogen, while using less steam. The CDCL system uses a two-stage moving bed fuel reactor with coal introduced after partial combustion in a preliminary reaction vessel in oxygen plus carrier gas (nitrogen or CO_2). Both concepts were viewed as having merits.

In the USA, at the Ohio State University at Columbus, Fan and others (2008) have been developing chemical looping processes including a syngas chemical looping (SCL) cycle using an iron-based carrier that appears somewhat similar to the Canadian SCL combustion cycle described by Gnanapragasam and others (2009), but without using pairs of reactors in series. These workers are themselves looking at a Coal Direct Chemical Looping (CDCL) that is also related to the one referred to above, except that the coal and oxygen are fed to the fuel reactor directly without the use of a pre-reaction vessel (Figure 22). The 'combustion reactor' (where the Fe_3O_4 is reconverted to Fe_2O_3) would be a fluidised bed system. The hydrogen reactor would be a moving bed system. Continuation of this work, including experimental studies, is reported in Li and others (2009a, 2010).

Laboratory studies for similar reaction schemes are being conducted at the University of Cambridge, UK. A small fixed bed reactor has been used in up to ten reduction/oxidation cycles of Fe-based carriers prepared by different methods (Bohn and others, 2009). Reduction of the Fe_2O_3 as far as elemental Fe is undesirable, resulting in low H_2 yield, so use of supports containing Al, Mg, or Cr, prepared by treatment of the Fe_2O_3 with the aqueous nitrates, was tested, and also compared with use of a silica-based support. Cr or Mg incorporation at 0.3 mole fraction or Al at 0.1 were effective, the latter being best, giving nearly 90% conversion of steam to H_2.

Laboratory tests for related partial oxidation with hydrogen production schemes are also being conducted in Japan. Hatanaka and others (2010) used Taiheiyo coal in a fixed and fluidised bed reactor (20 mm ID) to reduce a carrier consisting of iron oxide supported on alumina. A steam-nitrogen mixture was passed through the bed of mixed solids at temperature ranges from 723 K to 973 K, then a low O_2 nitrogen mixture (5–13% O_2), similar to depleted air from a combustor or gas turbine, used to burn off unreacted and deposited carbon. It was found that the rate of production of CO_2 was greater when the reactor operated as a fluidised bed than when it was a fixed bed. H_2 was formed in a relatively early phase of the reaction when the reactor operated as the fluidised bed.

Another example of related work for hydrogen production (at the University of Newcastle, UK) is on the use of mixed metal perovskites as carriers for cycles using CO as the reducing agent and steam as the oxidising agent, so that hydrogen is produced in an overall chemical looping water gas shift reaction (Murugan and others, 2010).

Alstom are developing a flexible looping system incorporating both a $CaSO_4$/CaS oxygen and a $CaCO_3$/CaO CO_2 loop. The US DOE is supporting the development programme at Windsor, Connecticut, USA. A 65 kWth pilot plant was completed in October 2008 and the next phase is a 3 MWth system, construction of which is due to begin in April, 2010, with first tests to be reported in June 2011. Future applications include steam plants, including retrofits, and gasification/syngas/liquids production. An identified requirement is that much better control of feeding and distribution of solids to the fuel reactor is needed for chemical looping than for CFBC. Commercialisation around 2020 is foreseen (Andrus and others, 2010).

Another example of an oxygen carrier chemical system that is not based around oxide production and decomposition is that proposed by Wang and Anthony (2006). Their system uses $CaSO_4$ to combust CO to CO_2. The carrier is reduced to CaS, and the latter is reconverted to $CaSO_4$ by high temperature reaction with air in another reactor, releasing heat. The CO is produced by coal gasification in a separate reaction vessel in an atmosphere of recycled CO_2. The CO_2 stream from the process would have a relatively low water content. All three reactors could use fluidised bed systems. Simulations indicated the importance of careful temperature selection: higher temperatures increase reaction rates, but a suitable difference in temperature between the oxidation and gasification reactors is needed for adequate heat transfer to the latter. However, higher temperatures encourage sintering of $CaSO_4$, causing deactivation, and encourage an undesirable side reaction between CaS and $CaSO_4$ to produce SO_2. Operation of the process at elevated pressure (1 MPa) could be used to suppress the latter reaction (Wang and Anthony, 2006).

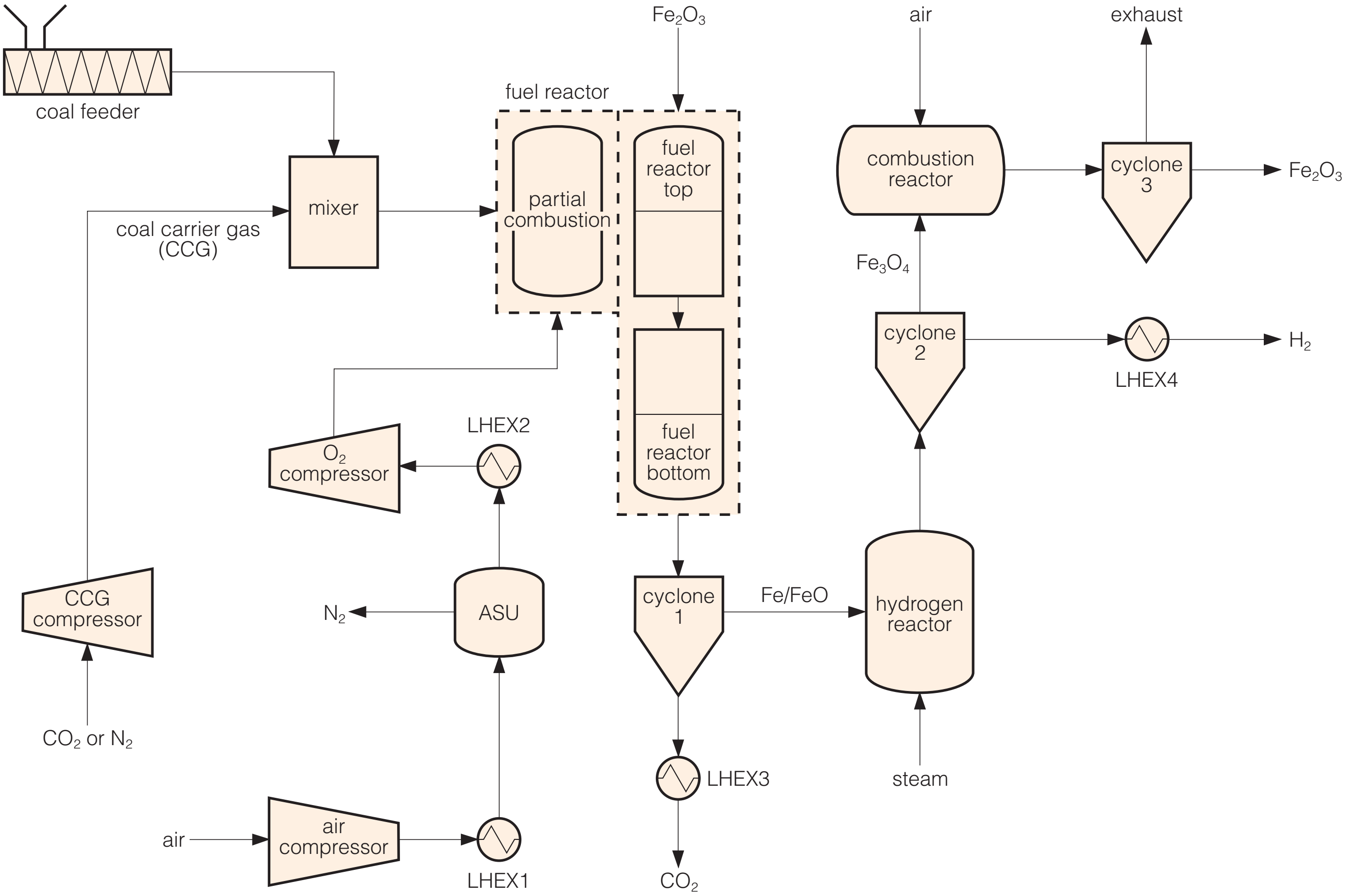


Figure 21 Coal direct chemical looping (CDCL) cycle concept of University of Ontario Institute of Technology (Gnanapragasam and others, 2009)

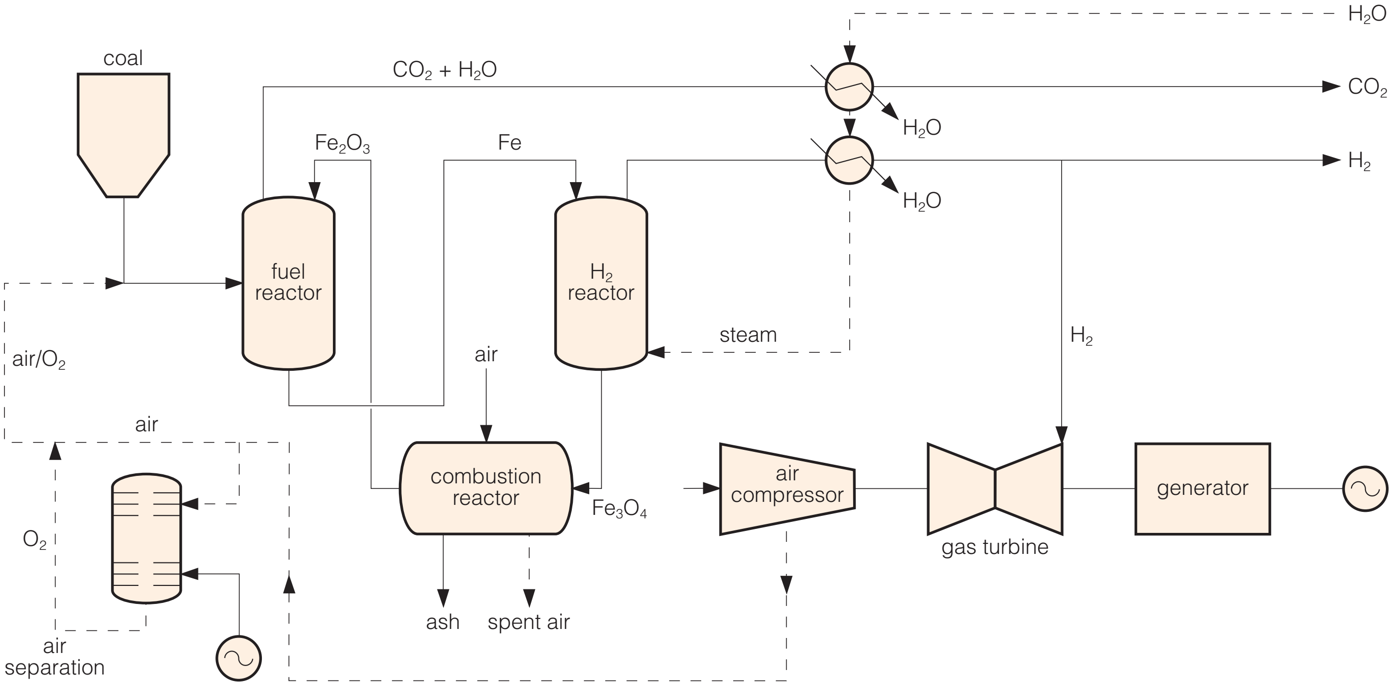


Figure 22 Coal Direct Chemical Looping (CDCL) cycle concept of Ohio State University at Columbus (Fan and others, 2008)

6 Power generation cycles

CLC combustion of coal will probably be used in various different power generation and other energy supply systems that capture CO_2. The main driving force is the prospect of greater efficiency with the near elimination of energy penalties of CO_2 separation, even at close to 100% CO_2 capture. The only significant CO_2 capture penalty will come from compression before storage. Where combined cycles are used, the CLC system will need to operate at elevated pressure, at perhaps 10–20 MPa, although there have been very few CLC tests at pressure. This chapter describes some example cycles for both gaseous and solid fuels.

Jin and others (2009) assessed the performance of a proposed coal gasification chemical looping combined cycle incorporating air saturation (*see* Figure 23). The efficiency was predicted to be as high as 51.3% (basis not given, presumed LHV), which was 5–10% points higher than conventional IGCC because of the thermodynamic advantage. The efficiency advantage compared with IGCC with pre-combustion CO_2 capture would be even greater. The carrier proposed was NiO on $NiAl_2O_4$, for which reactivity with syngas would be much greater than with methane because of the exothermic nature of the fuel reactor reactions (it is endothermic for methane). Novel CLC power cycles, one using hydrogen fuelling, and the other involving methanol-fuelled chemical looping combustion integrated with use of solar heat were also suggested (Jin and others, 2009).

VTI workers in Russia have found that, in CLC cycles incorporating initial coal gasification, the achievable efficiency of CO_2 capture will be limited to 91%. This is attributable to the presence of some nitrogen in the fuel gas feed to the CLC fuel reactor and also to the potential for CO breakthrough before combustion (Ryabov and others, 2009).

Tan and Santos (2006) describe a methane-fuelled CLC combined cycle using recirculating beds. Efficiencies of 45% and >55% were predicted, for gas turbine inlet temperatures of 900ºC and 1200ºC, respectively. The gas turbine on the air reactor outflow would produce the bulk of the power. Supplementary firing is suggested for raising the inlet temperature even higher, but would reduce net CO_2 capture (Tan and Santos, 2006).

Figures 24 and 25 show two natural gas CLC combined cycles, among those simulated by workers in Sweden as part of the ENCAP EU project (Lebas and others, 2006). The first

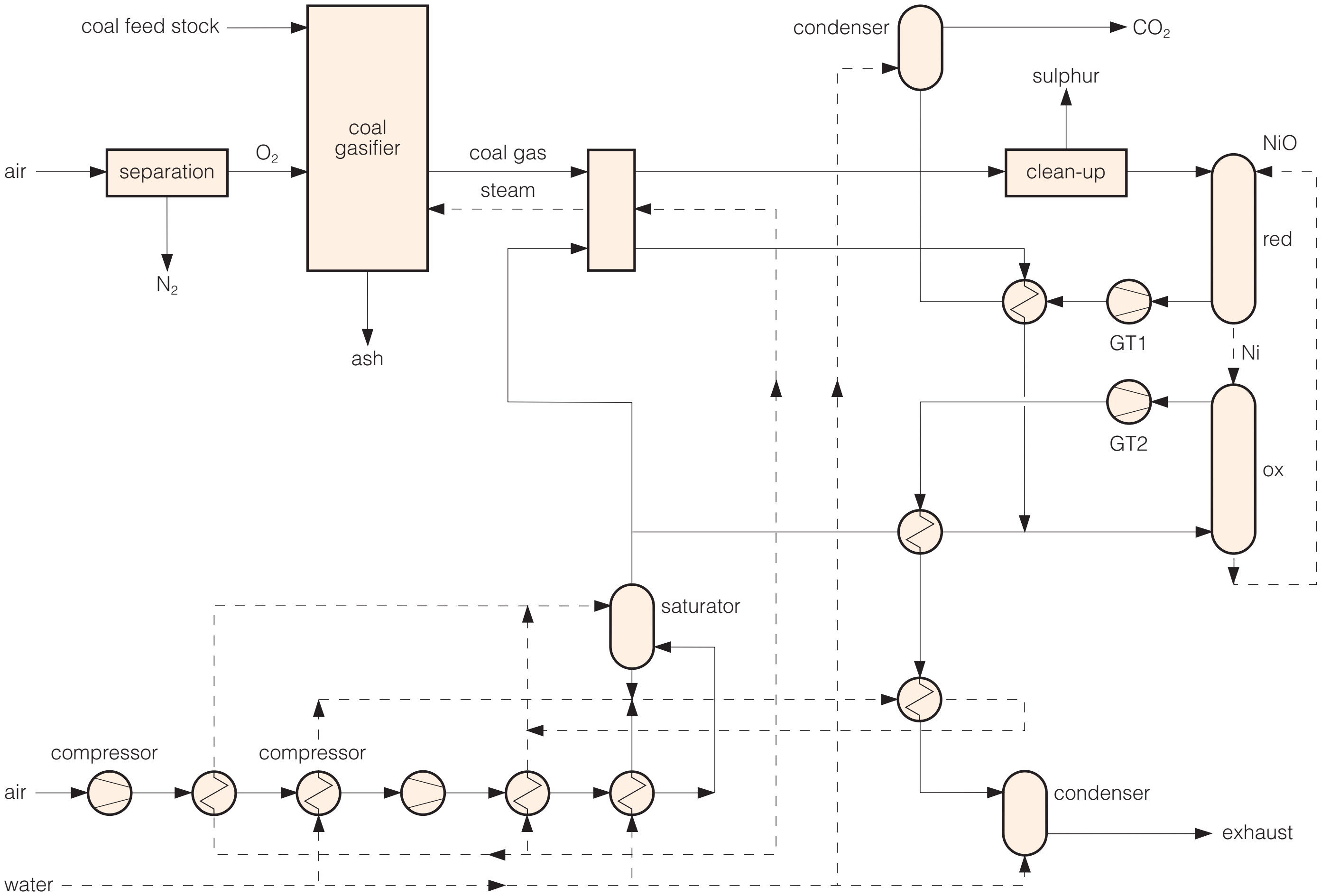


Figure 23 Coal gasification chemical looping combined cycle incorporating air saturation (Jin and others, 2009)

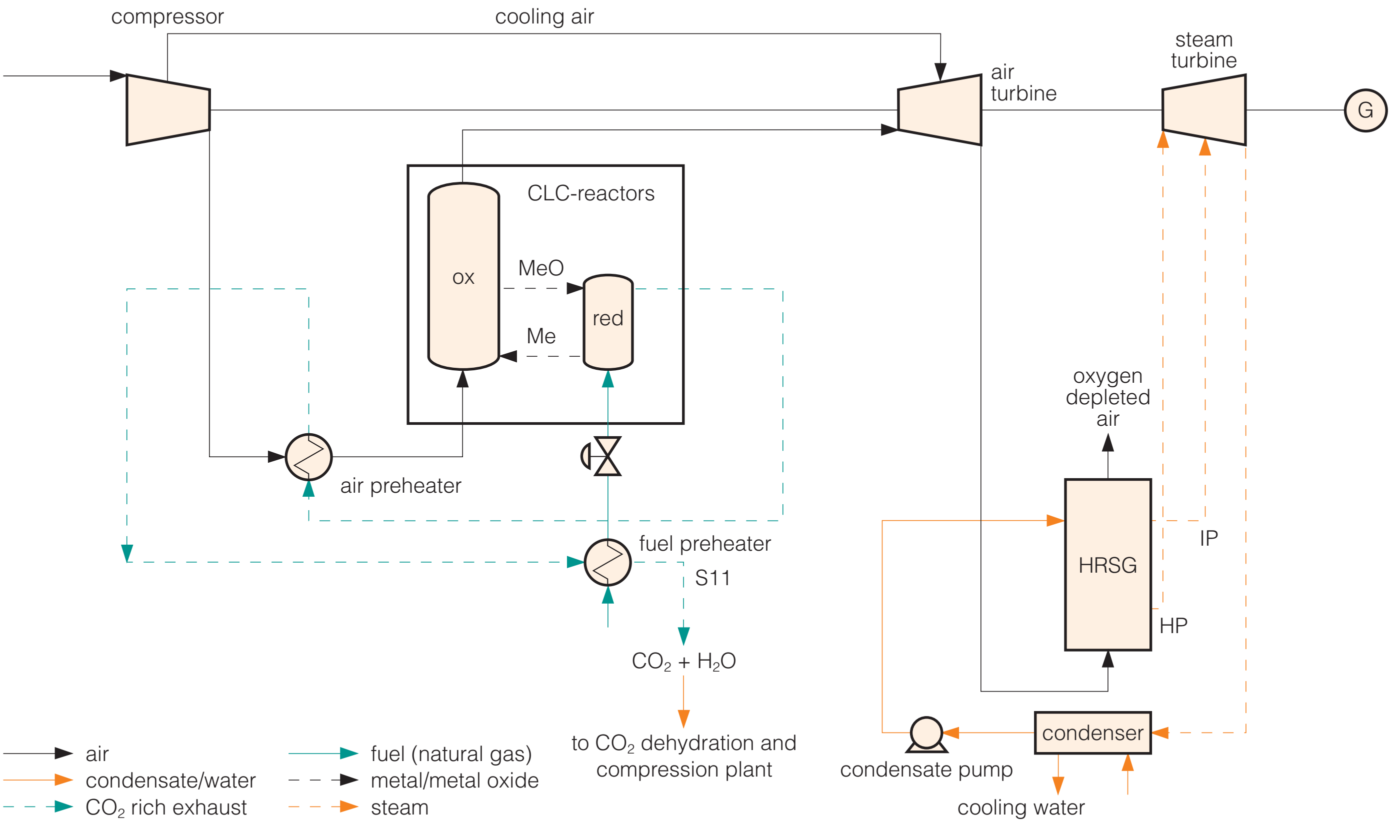


Figure 24 CLC combined cycle with exhaust heat recuperation from ENCAP EU project (Lebas and others, 2006)

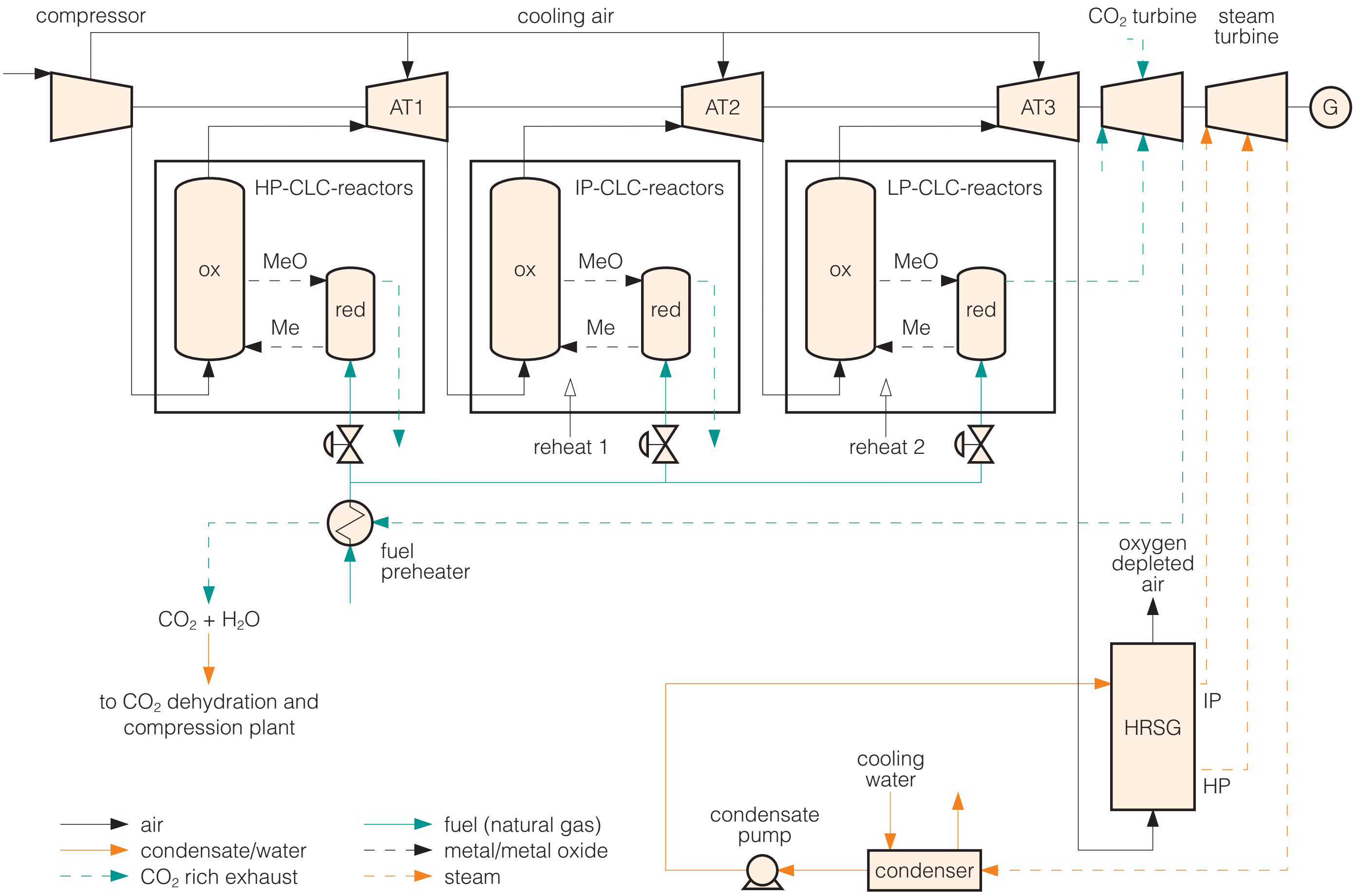
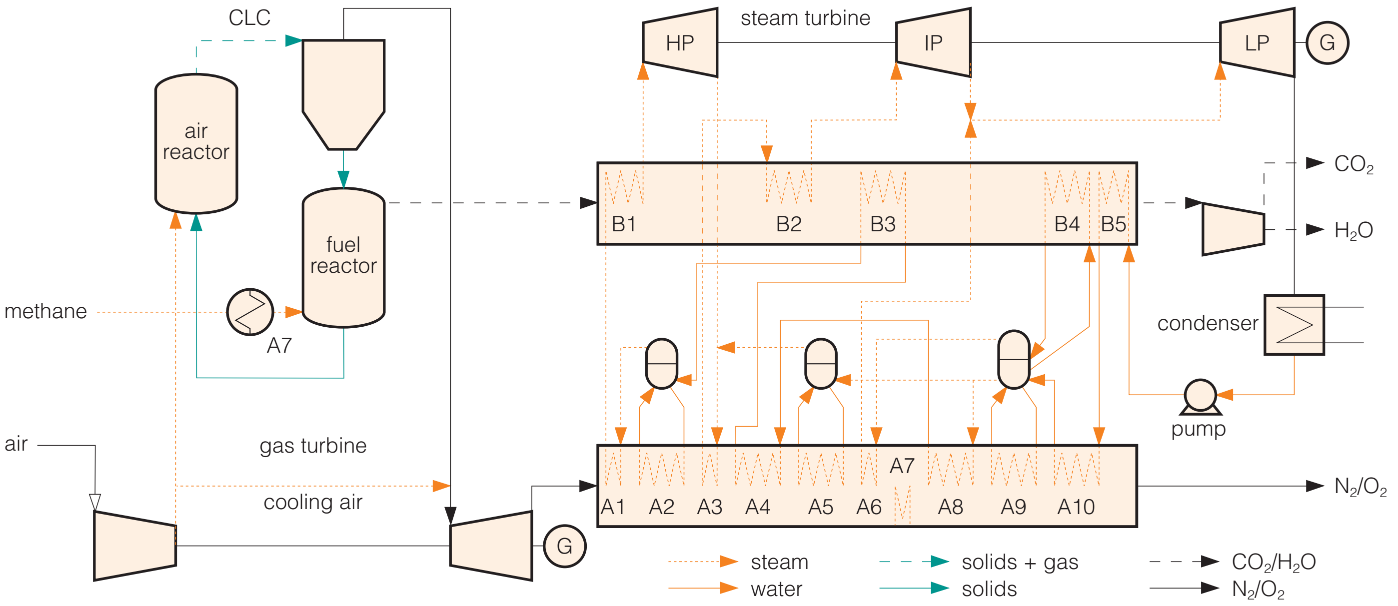
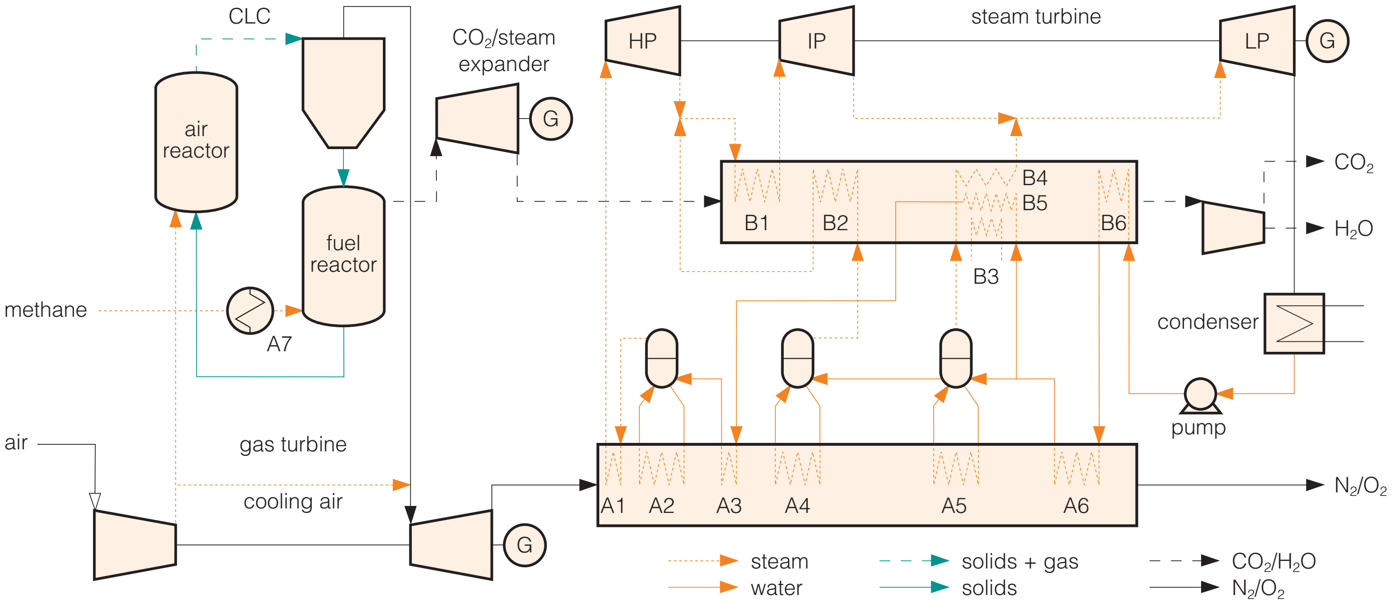


Figure 25 Double reheat CLC combined cycle from ENCAP EU project (Lebas and others, 2006)



A1, A3, A6 = superheater; A2, A5, A9 = evaporator; A4, A7, A8, A10 = preheater; B1, B2 = superheater; B3 economiser
B4 = supplemental evaporator; B5 preheater; G = generator

Figure 26 Combined cycle with CLC for CO_2 capture (Wolf, 2004)



A1, A3, A6 = superheater; A2, A5, A9 = evaporator; A4, A7, A8, A10 = preheater; B1, B2 = superheater; B3 economiser
B4 = supplemental evaporator; B5 preheater; G = generator

Figure 27 Combined cycle with CLC for CO_2 capture extended with a CO_2 expander (Wolf, 2004)

uses recuperation of the heat from cooling the fuel reactor outflow (CO_2 and H_2O) to preheat the compressed air from the gas (air) turbine for feeding the air reactor. Remaining heat in the CO_2 stream heats the natural gas fuel. The air turbine expands the depleted air outflow from the air reactor. The other cycle has reheat of the depleted air in two additional CLC air reactors with expansion through multiple stages of the air turbine. The fuel reactor outlets are expanded through a CO_2 turbine. Both cycles use further heat recovery to raise steam for the steam turbine. The additional complexity of the double reheat cycle results in a higher predicted efficiency. All CLC cycles were higher in efficiency than NGCC with CO_2 capture and the part load performance was also predicted to be better for the CLC cycles (Lebas and others, 2006).

Also in Sweden, Wolf evaluated natural gas-fired combined cycles with chemical looping combustion in two alternative configurations (Wolf and others, 2001; Wolf, 2004). In the first, the fuel reactor outlet stream (CO_2 and H_2O) would be passed through a steam generator while still at pressure (Figure 26), while the other incorporated an expander on this stream, before its use in the bottoming cycle (Figure 27). Both also incorporated steam generation from the outlet gas from a turbine that expands the air reactor gases. Both had a fuel input close to 800 MWth. The two systems (of around

400–450 MWe, net) were predicted to have similar efficiencies of 52–53% on a net, LHV basis, for turbine entry temperatures of 1200ºC. The CO_2 expander cycle developed more power, but it required more energy to recompress the CO_2 for liquefaction and storage. It was also possible to make better use of the heat (for evaporation) in the CO_2/H_2O stream from the simpler cycle. The calculations thus indicated that the additional cost of the more complex cycle (with CO_2 expander) would not be worthwhile. Use of methane in a topping combustor to achieve the 1200ºC air turbine temperature would not be as good a solution for maximising efficiency as designing the air reactor and carrier to operate at that temperature.

Wolf also compared the performance of nickel- and iron-based oxygen carriers in the cycle without the CO_2 expander (Wolf, 2004; Wolf and others, 2005). This work showed that the efficiency of the cycle was almost the same for the two carriers, provided that the material would withstand a temperature of 1200ºC. Pure haematite would agglomerate at below this temperature and so it would need to be stabilised with a material such as alumina. Such a material had been shown to be sufficiently resistant to agglomeration or degradation at 950ºC, but had not then been tested at 1200ºC. In both these literature sources, there is also extensive derivation and description of the pressurised reactor design data using hydrodynamic analyses.

Ryabov and others (2009) also refer to the importance of using adequately high temperatures in CLC reactors to realise high efficiencies from a combined cycle, suggesting 1000–1050ºC as needed.

The part load performance of a different natural gas fired combined cycle with chemical looping including a CO_2 expander has also been assessed (Naqvi and others, 2007). In this case, the expanded CO_2 was used to preheat the natural gas fuel feed to the CLC system. It was found that the net base load efficiency of 52.2% (LHV basis) decreased by 2.6 percentage points when the output was reduced to 60%. This was better than for a conventional natural gas-fired combined cycle. However, a complex control strategy would be required to achieve a successful system. The principal requirement would be to maintain equalisation of the pressure at the outlets of fuel reactor and air reactor to prevent CO_2 leakage.

In Korea, Park and others (2009) have presented the results of a comparison of natural gas and syngas-fuelled chemical looping combustion combined cycle (CLC-CC) plants for power generation. Aspen Plus was used to simulate the CLC-CC plants, sized at 100 MWth (around 50 MWe), and assumed to use fluidised bed reactors and an NiO/bentonite oxygen carrier. However, the flow sheet was not shown. The net efficiencies were calculated, for the natural gas fired plant and the syngas-fuelled plant, at 53.2% and 54.1%, respectively (fuel calorific value basis not stated). The oxidation reactor temperature assumed was 1200ºC and the reduction reactor temperature was 980ºC. Electricity costs were also estimated. The cost of electricity of the natural gas-fuelled CLC-CC plant was 5.8 ¢/kWh and that of the syngas-fuelled CLC-CC plant was 8.0 ¢/kWh .

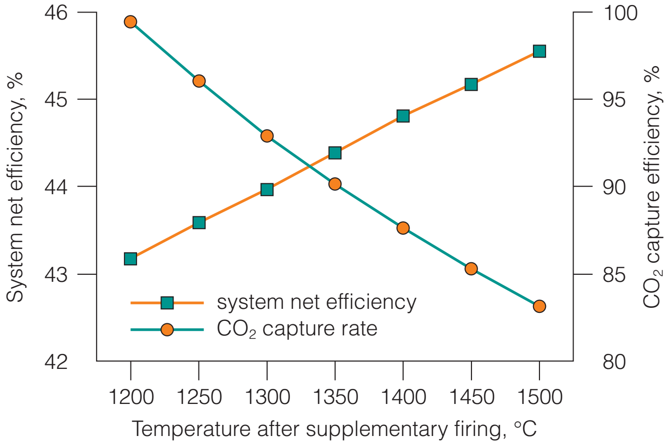


Figure 28 Predicted performance of novel coal gasification CLC combined cycle (Xiang and others, 2008)

At Southeast University, Nanjing, China, a novel advanced cycle incorporating pressurised coal gasification (a conceptual 'pipe-type' gasifier), syngas CLC and a gas turbine combined cycle has been proposed. The gasifier would be immersed in the air reactor of the CLC to enable it to utilise the heat developed in the air reactor. The proposed carrier is NiO. The pressurised (2.5 MPa) gasifier would be fed with a slurry of coal and sulphur sorbent, and the syngas would be cleaned in a cyclone then fed to the CLC fuel reactor. Compressed air from the two gas turbines would be sent to the air reactor, and the emerging heated vitiated air would be expanded through one of the gas turbines. The other gas turbine would be a CO_2 turbine, expanding the outflow from the fuel reactor. An Aspen Plus simulation of the cycle was assembled and used to assess the performance of the system. Because the assumed inlet temperature (up to 1500ºC) for the gas turbine on the air reactor outlet stream is higher than the air reactor outlet temperature (1200ºC), supplementary firing by some syngas is used to raise its temperature. This would limit the extent of CO_2 capture but increase efficiency. For supplementary firing of the CO_2 turbine, oxygen is fed to a catalytic combustor to combust residual CO and H_2. Several parameters were varied in the simulation and the effect on predicted performance calculated. Figure 28 shows that efficiencies of 43.2% and 45.5% (LHV basis) were predicted for CO_2 capture levels of 99% and 83%, and inlet temperatures at one of the gas turbines of 1200ºC and 1500ºC, respectively (Xiang and others, 2008).

Another paper from Southeast University, Nanjing, proposes a combined cycle involving solid fuels, this time with no gasifier but using direct CLC combustion of the solid fuel under pressure (Xiao and others, 2010). This would use the spouted fluidised bed fuel reactor that is being tested there also, and reported in Sections 4.2 and 8.1 of this report. The proposed system (PCLC-CC) is shown in Figure 29. No predicted efficiency value was given. An air turbine, expanding depleted air from the air reactor, and a CO_2 turbine, expanding the fuel reactor outlet, are used, as in the proposed gasification and the natural gas CLC combined cycles described earlier in this section. Laboratory-scale work to evaluate the use of iron oxide as a carrier under pressurised conditions is being carried out and was reported in Section 3.2 (Xiao and others, 2010).

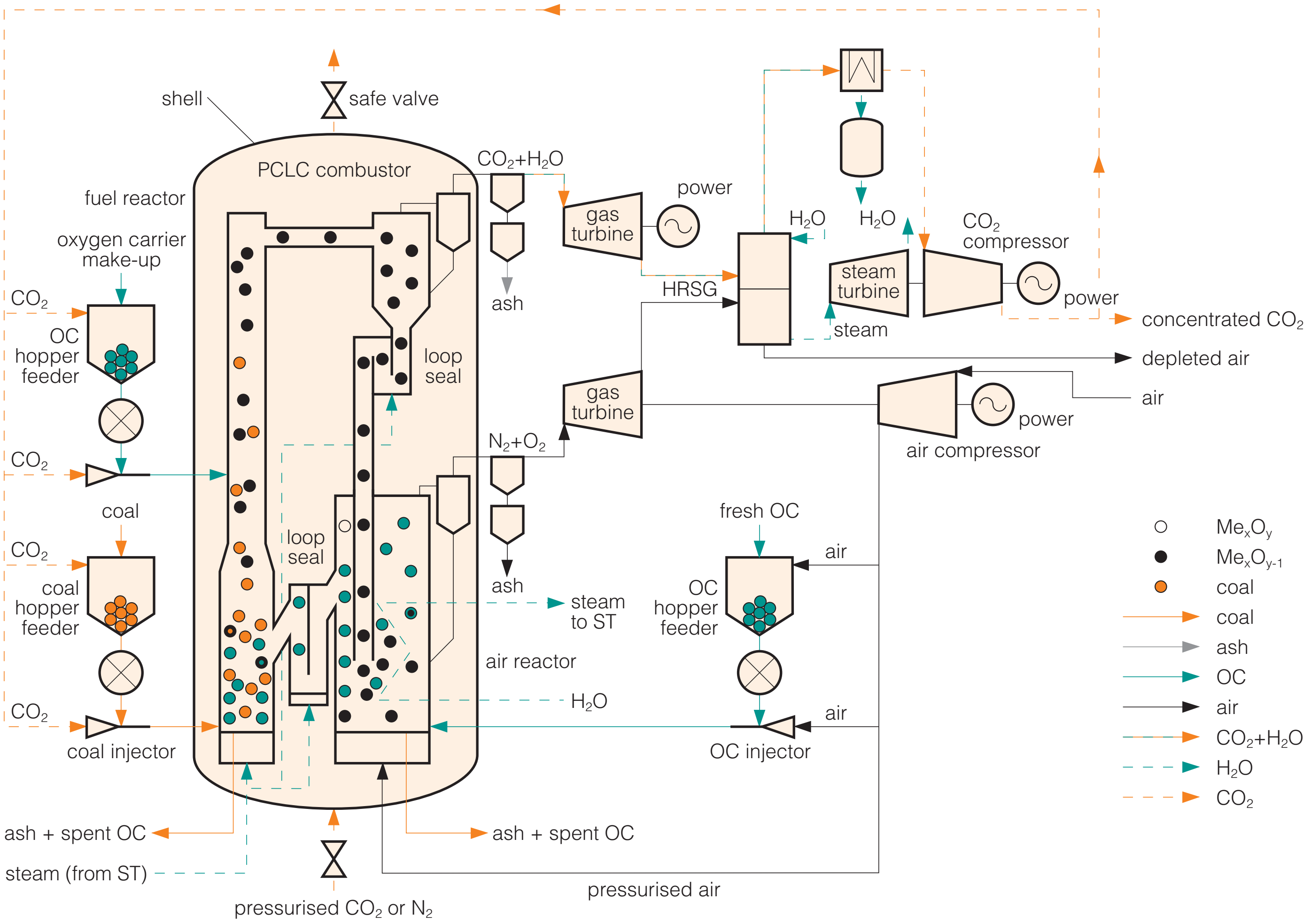


Figure 29 Combined cycle using direct CLC combustion of coal in a pressurised spouted fluidised bed reactor (Xiao and others, 2010)

As part of the EU RFCS ECLAIR project, simulations have been carried out of a system based on the EU ENCAP project 450 MW coal-fired CLC plant configuration based around commercial CFBC components. The simulations indicate that minimising the flow of fluidising steam to the fuel reactor, if necessary adding hot, in preference to cold, recycled CO_2, would be best in order to optimise generation efficiency. An inadequate conversion in the fuel reactor could be compensated by increasing the efficiency of the carbon stripper. A net electrical generating efficiency of 41.2% (LHV), was estimated for 90% CO_2 capture, for which carbon conversions between 70% and 90% (once-through basis) would be usable. Higher degrees of CO_2 capture would be possible but reduce efficiency (Fillman and others, 2010).

According to one major supplier of power generation equipment (Alstom), utility direct-fired coal CLC plants will need new advanced control systems and will require pulverising of coal, not just the crushing familiar in conventional CFBC. Potential issues include erosion and defining the best plant configuration for best heat utilisation. In addition, means to achieve grid response will need to be identified and developed. Only systems using natural carrier materials are of interest to Alstom because of supply and cost issues. They consider the likely earliest timescale to deployment of CLC technology at utility scale is 2025–30 (Pfeffer, 2010).

7 Effect of impurities in fuels

It is important in chemical looping systems that the fate of impurities in the fuel, especially sulphur compounds, is understood because it may affect the process in two different ways. Theoretical studies indicate that reaction of the sulphur species with the oxygen carrier may give rise to poisoning of the carrier, degrading the efficiency and economics of the process. Nickel-based oxygen carriers may be particularly affected, and the resulting sulphides could also have low melting points, which may cause agglomeration, and so present fluidisation difficulties in a CLC process using such systems. The sulphur may also end up being converted to SO_2 in the air reactor, and/or it may appear in the fuel reactor's outlet stream as a contaminant of the CO_2. Either occurrence may necessitate incorporation of desulphurisation systems.

Workers at CSIC, Zaragoza, Spain, have recently used a 500 Wth interconnected fluidised bed CLC system to test in practice the effects of sulphur compounds in methane fuel, using as carrier NiO impregnated on γ-Al_2O_3 (García-Labiano and others, 2009; Adánez and others, 2009b). The apparatus, which uses the usual bubbling bed for the fuel reactor, is shown in Figure 30. The solids inventory of the system was 1.3 kg. The main properties of the carrier are shown in Table 20. H_2S was incorporated with methane at different concentrations. Test conditions are given in Table 21. Nickel compounds containing sulphur (mainly Ni_3S_2) were formed under all the test conditions, even where not expected to be thermodynamically favoured from initial considerations. Consequently, SO_2 was detected in the outlet stream of the air reactor as these compounds reacted with the oxygen in the air. A revised consideration of the potential reactions and thermodynamics indicated that the sulphidation of the carrier was linked to the presence of CO and H_2 in the fluidised bed. Small quantities of H_2S and SO_2 were also detected at the outlet of the fuel reactor, indicating that, among the reactions occurring could be formation of $NiSO_4$ in the air reactor, followed by its reaction with hydrogen in the fuel reactor. Samples of the carrier taken from the system after each regeneration step showed that the oxygen carriers did recover their initial reactivity after a period in the absence of H_2S introduction.

In further investigations using the same CLC apparatus, again on methane fuel, upon introduction of 500 ppm(v) of H_2S in the methane, analysis of the outlet gases from the fuel reactor showed that CO_2 production decreased and some unconverted methane appeared after approximately ten minutes, while the CO and H_2 concentrations increased slowly to 1.5 and 3 vol% respectively (Adánez and others, 2009a). Again, SO_2 was detected in the gases exiting the air reactor, and again the inference from this was that oxygen carrier deactivation was being caused by the formation of nickel sulphides. Mass balance calculations indicated a gradual accumulation of sulphur in the carrier particles. Some SO_2 again appeared in the fuel reactor exit stream also. The broad conclusion was that the best way to avoid efficiency decrease, SO_2 emissions and sulphur gases contamination of CO_2 streams would be to desulphurise the fuel gas to approximately 100 ppm (García-Labiano and others, 2009; Adánez and others, 2009a).

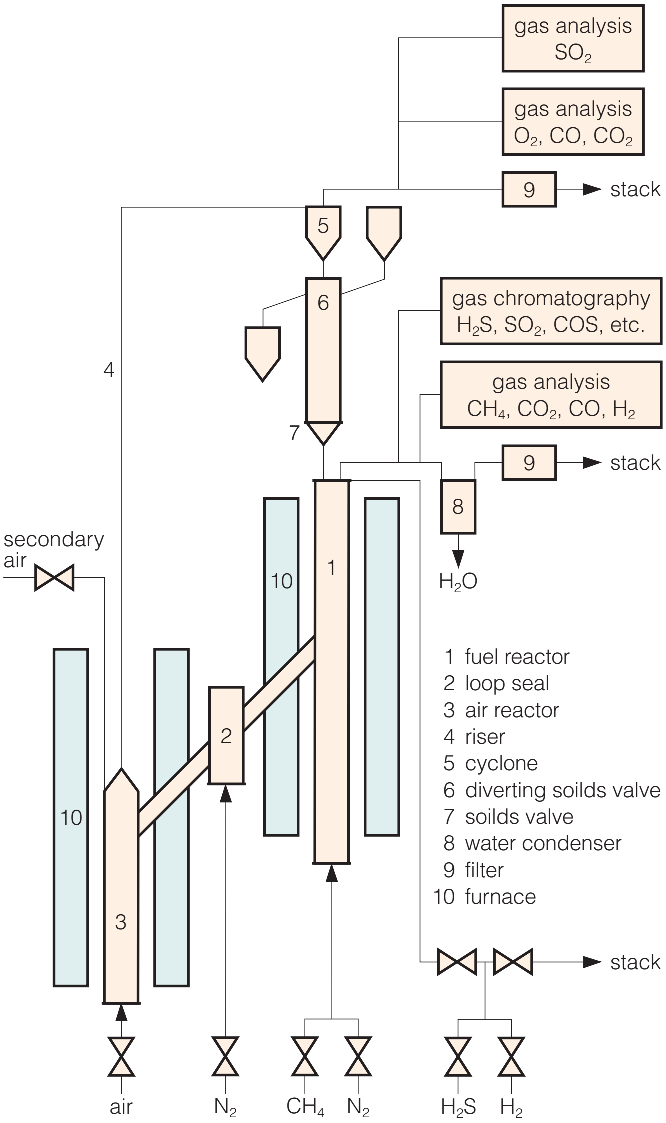


Figure 30 500 Wth fluidised bed CLC system at CSIC, Zaragoza, Spain (García-Labiano and others, 2009)

Table 20 Characteristics of a NiO-γ-Al_2O_3 carrier used in tests at CSIC, Spain, of the effect of sulphur compounds in methane fuel for chemical looping (García-Labiano and others, 2009)

NiO content, wt%	19
Particle size, mm	0.1–0.3
Particle density, kg/m³	2500
Mechanical strength, N	4.3
Porosity, %	41.7
BET surface area, m²/g	6.8
Oxygen transport capacity	0.04

Table 21 Test conditions used in assessments of the effect of sulphur compounds on chemical looping of methane at CSIC, Spain (García-Labiano and others, 2009)

Test	Temperature in fuel reactor, ºC	Temperature in air reactor, ºC	CH_4, vol%	H_2S, vppm	Whether conditions thermodynamically favoured nickel sulphides formation
0	870	950	30	0	
1	870	950	30	0 (500)	no
2	870	950	30	500	no
3	870	950	30	300	no
4	870	950	30	100	no
5	870	950	30	300	yes
6	870	950	30	800 (1000)	yes
7	870	950	30	300 (800)	yes

The CSIC workers have reported similar work using Cu-based carriers supported on alumina (Forero and others, 2010). The presence of H_2S did not produce a decrease in the combustion efficiency at oxygen carrier to fuel ratios above 1.5, even at 1300 ppm(v) H_2S. In contrast to the Ni-based carrier, over 95% of the sulphur was released in the outlet of the fuel reactor as SO_2. The main issue in this case will concern the CO_2 quality requirements for transport and storage. Formation of Cu_2S was not an issue except at lower carrier to fuel ratios, but there were no resultant agglomeration problems in the fluidised bed.

As reported in Section 3.1, Polish and American work showed that, for carriers based on Fe_2O_3-MnO_2 supported on ZrO_2 and sepiolite, H_2S in simulated syngas did not affect oxygen carrying capacity or reaction rate and there was no detection of sulphides, sulphites or sulphates (Ksepko and others, 2010a). They also investigated NiO carriers on various supports using a TGA and syngas as fuel, both with and without H_2S added. During five reduction-oxidation cycles, it was found that the NiO/SiO_2 showed a decrease in oxygen transfer capacity with H_2S addition, but that sepiolite, ZrO_2, or TiO_2-supported NiO maintained its capacity. NiO/SiO_2 also showed the lowest reduction and oxidation rates. It was concluded that sepiolite was a promising support for low-cost and stable NiO oxygen carriers for coal-derived synthesis gas (Ksepko and others, 2010b).

A 1 kWth PDU CLC with a spouted bed fuel reactor at Southeast University, Nanjing, has been used to investigate the effect of sulphur in coal (Shenhua – *see* Table 19 page 31) on a nickel-based carrier. Steam was used as fluidising agent. It was found that a greatly increased char conversion at higher temperatures had the beneficial effect of reducing the quantity of sulphur-containing char being conveyed to the air reactor, so reducing SO_2 production in that reactor. Only about half as much SO_2 was released from the air reactor at a fuel reactor temperature of 985°C, compared with at a fuel reactor temperature of 950°C. SO_2, H_2S and COS were produced in the fuel reactor. Ni_3S_2 was also formed in the fuel reactor by reaction of some of the H_2S with Ni, and the Ni_3S_2 was the agent for transport of sulphur to the air reactor (Shen and others, 2010). Note that the general consensus is that NiO carriers seem unlikely to be used for coal CLC. The Nanjing group are also looking at iron ore carriers.

The solid waste from CLC of coal would consist of a mixture of oxygen carrier particles that are too small to be retained plus fine ash. Gao and others (2008) have suggested that waste from an NiO-based CLC system for coal combustion could be treated with nitric acid and the product nickel nitrate recycled to the NiO carrier preparation process.

A similar method for treatment of elutriated Cu-based carrier fines from CLC of methane in the 10 kWth CLC system at CSIC, Zaragoza, Spain, has been tested by García-Labiano and others (2007). The $Cu(NO_3)_2$ solution produced from nitric acid treatment of the fines (up to 80% recovery of Cu) was used in the preparation of new carrier material by wet impregnation of alumina. TGA tests on the new carrier showed that they performed well. The solid residue after copper extraction was shown to consist mostly of alumina and $CuAlO_2$, and said to be suitable for safe disposal.

8 Conclusions

This report has looked at chemical looping combustion (CLC) and related concepts for using carbonaceous fuels in energy production. The technology is being developed as a possible way to CO_2 capture with reduced energy consumption. The value of CLC is in the prospect of greater efficiency, with the near elimination of energy penalties of CO_2 separation, even at close to 100% CO_2 capture. The focus here has been to investigate progress in its application to coal and coal-derived syngas, although some work with natural gas is included. Early commercial deployment is likely to be at around 20 MWth for steam production, using natural gas fuel. Researchers working on chemical looping combustion and related systems are active in a number of countries, including Austria, Canada, China, Germany, Japan, Korea, the Netherlands, Russia, Spain, Sweden, the UK and the USA.

There are many different variants of CLC, but a common feature is that an oxygen-containing solid material supplies the oxygen to a fuel, and the spent oxygen carrier is re-converted to its higher oxygen content form by high temperature reaction in an air stream. Mechanical arrangements keep the oxygen-absorbing and oxygen releasing reactions separate, so there is no direct contact between air and fuel, CO_2 recovery is thus simplified, and there is potential for higher efficiency in power cycles. NOx emissions are also low, because the temperature in the oxidation (carrier regeneration) reactor is lower than in conventional combustion flames.

Suitable carriers include oxides of Ni, Mn, Cu and Fe. Nickel oxide on various support materials has been most explored, but is best for gaseous fuels (natural gas or clean syngas). Low priced, minimally processed materials are best suited as oxygen carriers for CLC of coals. Examples are natural haematite or oxide scale from steel rolling mills (forms of Fe_2O_3) and ilmenite ($FeTiO_3$).

The cyclic nature of chemical looping means that interconnected fluidised bed systems are well suited, as they provide the necessary residence time and good solids/gas contacting for oxygen absorption and release as well as ready and efficient disengagement of the solids from the gas streams with cyclones. For solid fuels, the system design also needs to incorporate means for effective separation of ash for disposal. Heat transfer between reactors is important in a practical system and this can be accomplished by using the recirculating oxygen carrier to do this.

First studies of chemical looping combustion were in laboratory apparatus, using methane, carbon monoxide, or carbon monoxide/hydrogen mixtures as fuels. Progression to proof of concept in small continuous systems based on fluidised beds followed. The scale of the technology on gaseous fuels has now reached around 120 kWth. Direct CLC of coal was also first shown in laboratory apparatus and, more recently, in continuous fluidised bed process development units. Previous tests have been at up to around 10 kWth, but a 1 MWth plant has recently been commissioned.

It has been difficult, so far, to achieve close to 100% conversion of solid fuels. One research group found a maximum of 95% conversion of coal in 4–15 minutes, using ilmenite as carrier in batch reduction-oxidation cycles. Some single TGA tests have indicated complete combustion, but, in continuous or repeated tests, around 10% of the carbon has frequently remained in the form of CO. However, tests using solid fuels are still at a fairly early stage.

Continuous tests in a 10 kW capacity process development unit in Sweden at 3.3 kW coal feed rate gave 50–80% fuel conversion, using an ilmenite carrier. However, this was probably because the small scale of the work restricted the performance of fuel recycle systems. CO_2 capture was in the range 82–96%, but a larger, well-optimised carbon stripper was considered likely to give higher performance. A Chinese spouted bed continuous system of similar scale, operated at around 8 kW fuel input, gave a maximum 92.8% coal conversion with an 80% CO_2 capture efficiency, using a NiO-based carrier. The slightly disappointing conversion performance was again attributed to the scale of the apparatus. In a 1 kWth PDU, a haematite carrier at a fuel flow of 0.7 kW gave a conversion of 82–87% and a CO_2 capture efficiency of about 85%. Ash separation was not demonstrated in these initial proof-of-concept continuous tests.

One method devised to obtain much greater reaction rates for coal CLC is chemical looping with oxygen uncoupling (CLOU). In this case, use of a carefully chosen carrier and appropriate conditions enables the oxygen to be liberated in gaseous form before it reacts with the solid fuel. An example is CuO at temperatures at which it is reducible to Cu_2O, rather than the element. Complete conversion of carbon to CO_2 in a commercial CLOU unit has been predicted, and the technique should lead to a system requiring a smaller oxygen carrier inventory, so reducing costs.

CLC tests at up to 1 MWth will start shortly at the continuous pilot plant that will use solid fuels that has been constructed at the Technical University of Darmstadt, Germany in an EU-funded collaborative project. After that, the next stage in scale-up is expected to be to 10–50 MWe, but results from the 1 MWth plant will also feed into a design study for a 450 MWe coal-fired CLC system based around commercial CFBC components. Simulations of the latter indicate a net electrical generating efficiency of 41.2% (LHV), for 90% CO_2 capture, for which carbon conversions between 70% and 90% (once-through basis) would be usable. Higher degrees of CO_2 capture would be possible but reduce efficiency.

Combined cycles could use CLC. Simulations of 400–450 MWe combined cycle systems fired on natural gas indicate efficiencies of 52–53%, net, LHV basis. Pressurised

CLC would be needed and there has, to date, been little experimental work at pressure. The temperatures needed in the CLC system to achieve these efficiencies would also be challenging. Topping combustion (supplementary firing) ahead of the gas turbine on the air reactor outlet stream would be an alternative, but reduce the extent of CO_2 capture.

The most straightforward way to use coal CLC in a combined cycle would be through coal gasification in a conventional gasifier followed by gas clean-up, then combustion of the syngas in the CLC fuel reactor. Evaluations of some cycles indicate potential efficiencies comparable with those stated above for natural gas CLC combined cycles. A CLC combined cycle incorporating direct coal CLC has also been proposed.

CLC configurations incorporating coal processing for both power and hydrogen production are being simulated. These cycles have greater complexity than IGCC polygeneration systems with CO_2 capture, but any CLC systems will involve new challenges. According to one major supplier of power generation equipment, direct coal-fuelled utility CLC plants will need new advanced control systems and will require pulverising of coal, not just the crushing familiar in conventional CFBC. Potential issues include erosion and defining the best plant configuration for heat utilisation. In addition, means to achieve grid response will need to be identified and developed.

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