

# PRELIMINARY ASSESSMENT OF A CARBON LOOPING COMBUSTION PROCESS (CarboLoop)

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## Abstract

The CarboLoop concept proposed by Salatino and Senneca [1] pursues the simple idea that a carbon-based fuel can act itself as oxygen carrier as it is cycled between an Oxidizer, where the fuel uptakes oxygen at moderate temperature (say 300-400°C), and a Desorber where desorption of surface oxides is accomplished in inert atmosphere at higher temperature (in the order of 700°C). Looping of the carbon fuel between the oxidizer and the desorber enables stepwise conversion of carbon over multiple cycles yielding a nearly pure stream of CO<sub>2</sub>, ready for sequestration, at the exhaust of the Desorber.

This study further contributes to the exploitation of the CarboLoop concept by reporting on the thermochemistry of the oxidation and desorption stages and by analyzing issues associated with energy integration between the Oxidizer and the Desorber. A calorimetric study on raw and pre-oxidized carbon samples indicates that carbon oxidation at temperatures in the order of 300-400°C is moderately exothermic, whereas a pronounced exothermicity is displayed upon exposure of the oxidized samples at higher temperature. The proposed mechanistic frame is based on the formation of “metastable” complexes upon exposure to oxygen at moderate temperature, followed by isomerization/rearrangement into “stable” oxides and subsequent desorption at higher temperature.

Thermochemical and kinetic data provide the basis for a preliminary layout of the CarboLoop process. Carbon inventory and circulation rate between the Oxidizer and the Desorber and thermal loading in either reactor are assessed with reference to an assigned thermal throughput and set of operating/design parameters.

## Introduction

Chemical looping combustion of solid fuels is rapidly gaining interest as a challenging capture-ready combustion technology. A method to overcome the inherent limitations of carrier-based looping combustion of solid carbons has been proposed by Salatino and Senneca [1-2]. The CarboLoop concept is based on the consideration of the well established role played by surface oxides as metastable reaction intermediates in the combustion of solid carbons [3-11]. A simple semi-lumped oxidation mechanism [12] may be helpful to understand the mechanistic

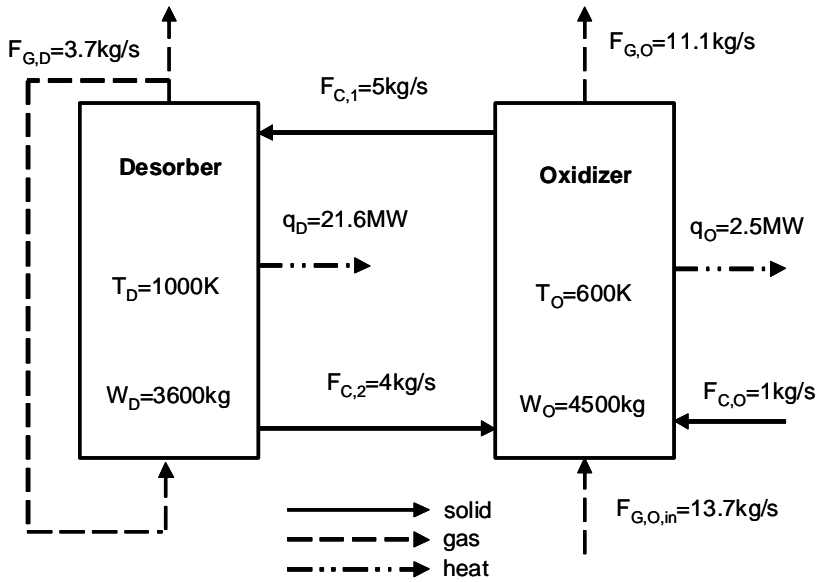


Figure 1. Outline of the CarboLoop process based on a dual bed reactor.  
Values refer to results of base case computations

basis of the CarboLoop:



The very basis of the CarboLoop concept is to exploit the differences in the reaction rates of the individual steps in scheme 1) as a function of temperature. At moderate temperature (say 300-400°C) oxygen chemisorption (step 1) progresses at an appreciable rate, whilst switch-over (reaction 2) and surface oxide desorption (reaction 3) are modest, being kinetically limited. At these temperatures it is possible to extensively uptake oxygen on carbon, with minimal release of gaseous carbon oxides. The oxidized carbon can eventually be exposed to higher temperatures, in the order of 700°C, so that oxygen complexes can be released as CO/CO<sub>2</sub>, according to step 3 in scheme 1). CarboLoop pursues the simple idea that the carbon-based fuel can act itself as oxygen carrier as it is cycled between an Oxidizer, (Fig. 1), where the fuel uptakes oxygen at moderate temperature, and a Desorber where desorption of surface oxides is accomplished in inert atmosphere at higher temperature. Looping of the carbon fuel between the oxidizer and the desorber enables stepwise conversion of carbon over multiple cycles yielding an almost pure stream of CO<sub>2</sub>, ready for sequestration, at the exhaust of the Desorber. A successful proof-of-concept of CarboLoop has been given by Salatino and Senneca [1-2] who simulated the cyclic fate of solid fuel by discontinuous

experiments in a thermogravimetric analyzer and assessed the kinetics and extent of oxygen uptake/carbon loss between the Oxidizer and the Desorber. Further assessment of the process is reported in refs [12-13].

Full exploitation of the CarboLoop concept requires energy integration between the Oxidizer and the Desorber, calling for detailed knowledge of the thermochemistry of the oxidation and desorption stages. Detailed thermochemical studies of individual steps of carbon oxidation are lacking and the subject has been recently addressed by the authors [14].

## Experimental

Experiments have been carried out on char from a South African bituminous coal. The char was prepared by pyrolyzing batches of coal for 5min in a lab-scale fluidized bed reactor at 800°C in nitrogen flow. Char samples were ground and sieved in size range 100-150µm prior to further processing. A complete set of experiments aimed at the characterization of the thermochemistry of oxygen chemisorption, including Temperature programmed desorption, differential scanning calorimetry and peribolic calorimetry, have been carried out on samples of the char, and are reported in ref. [14].

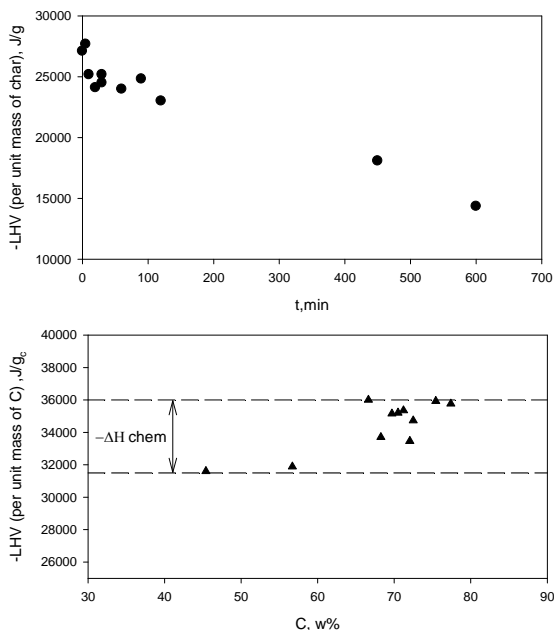
In the present paper only results of calorimetric measurement of the heat of combustion on raw and on pre-oxidized char will be presented. The char sample was dehumidified in a stove at 110°C overnight. Approximately 2 g of the sample were loaded in a pyrex reactor of 3cm ID and 5 cm height. The reactor was continuously flushed with air and heated up externally by electric ovens to the temperature of 300°C. The treatment was carried out for times ranging between 5 to 600min. The sample retrieved from the reactor after treatment was analysed by means of a LECO CHN 2000 elemental analyser to determine its carbon content and by means of a Parr 2000 isoperibolic calorimeter to determine its heat of combustion (LHV).

## Results and discussion

Figure 2 report results of calorimetric experiments. The rationale of this type of experiments is based on the relationship:

$$\Delta H_{\text{comb,raw}} = \Delta H_{\text{chemisorption}} + \Delta H_{\text{comb,preoxidized}} \quad (2)$$

according to which the heat of combustion of pre-oxidized samples equals the heat of combustion of the raw char samples minus the heat involved in oxygen chemisorption at moderate temperature. Figure 2A reports the LHV measured by the isoperibolic calorimeter of the raw char and of char after chemisorption of oxygen at 300°C, as a function of the duration of chemisorption. Notably the LHV per unit sample mass decreases from -28kJ/g of the raw char to -24kJ/g after 5 minutes of treatment. Eventually it decreases almost linearly with the duration of treatment up to 600min, when it reaches a value of -14kJ/g. It must be noted that prolonged heat treatment at 300°C resulted not only in oxygen uptake and formation of carbon-oxygen complexes, but also in some loss of carbon by partial



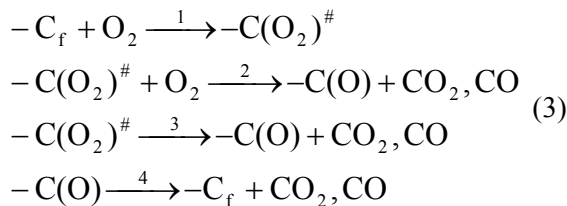
**Figure 2.** Heat of combustion of raw and pre-oxidized chars. Pre-oxidation performed in air at 300°C. upper diagram) -LHV as a function of duration of chemisorption; lower diagram) -LHV normalized by the actual char carbon content.

oxidation.

Accordingly, Figure 2B reports the LHV expressed per unit of actual carbon mass in the sample. The LHV of the raw char per unit mass of carbon is -36 kJ/gC, slightly larger than the theoretical heat of combustion of graphite, consistently with the partly amorphous nature of carbon and with the - limited - content of heteroatoms. A very abrupt decay of the heat of combustion is recorded after early chemisorption of oxygen, entailing only limited loss of carbon. The decay is less pronounced upon further oxidation at 300°C. A reduction of

the heat of combustion of nearly 4kJ/gC is determined after prolonged oxidation of char at 300°C, i.e. when extensive treatments saturate the oxygen uptake capacity of the char. According to eq. 2, this value could be regarded as the heat involved in oxygen chemisorption at moderate temperature, though minor contributions from oxidation of residual heteroatoms (e.g. H) present in the char after pyrolysis cannot be entirely ruled out. The heat of reaction involved at this stage is very modest. The LHV of the fully oxygen-saturated carbon approaches, instead, the much larger value of  $\Delta H = -31.5$  kJ/gC. This must be regarded, within a first order approximation, as the heat cumulatively associated with processes that ultimately result into desorption of surface oxides at high temperature.

Results can be interpreted in the frame of the following reaction scheme:



According to this mechanism, mild chemisorption at moderate temperature results in non-dissociative chemisorption of oxygen, with formation of a “metastable” surface oxide. The metastable oxide may further undergo complex switch-over in the presence of oxygen according to reaction 2. Alternatively, metastable oxides can be rearranged or isomerized into more energetically favourable forms, with possible release of gaseous carbon oxides, according to the exothermic reaction 3. Finally, reaction 4 represents the endothermic abstraction of CO and CO<sub>2</sub> from the oxidized carbon.

### Assessment of the CarboLoop process

A preliminary assessment of the CarboLoop process has been accomplished by computing the relevant mass/energy fluxes associated with steady operation of the process. Reference is made to the scheme in Fig. 1. Simplified material and energy balances around the two basic units are hereby reported for the case when a pure (ash-free) carbon fuel is processed, using air to oxidize the fuel in the O-reactor.

Base case computations of the relevant process variables have been carried out by selecting likely values for the model input variables. Reference was made to a 1kg/s carbon feed rate (LHV=30MJ/kg) corresponding to about 30MW nominal thermal power input.  $\Delta X$  has been set at 20%. Enthalpies of oxidation/desorption have been computed as:  $\Delta H_D = f \cdot LHV$  and  $\Delta H_O = (1-f) \cdot LHV$ , taking  $f=0.85$ . Excess air was fixed at  $e=1.2$ . Reactor temperatures are  $T_O=600K$  and  $T_D=1000K$ . The average carbon residence time  $\tau$  is set at 15min in both reactors.

Results of the computations are illustrated in Fig. 1. Thermal balance on the two reactors indicates that carbon oxidation in the Oxidizer is self-sustained, with moderate heat extraction ( $q_O=2.5MW$ ), whereas most of the heat release takes place in the desorber ( $q_D=21.6MW$ ). Of course this result is crucially influenced by the energetics of oxidation and desorption, and more specifically by the balance between the enthalpy of mild oxygen chemisorption at moderate temperature and that associated with reactions occurring at high temperature, like the stabilization by surface oxide rearrangement of the metastable complexes, and, eventually, desorption of surface oxides as CO and CO<sub>2</sub>.

### Conclusions

Looping combustion of solid carbon may be accomplished, according to the CarboLoop concept, by alternating carbon oxidation with air at moderate temperature and desorption of carbon-oxygen complexes at higher temperature in a dual interconnected fluidized/entrained bed reactor. A key issue is energy

integration between the oxidation and desorption stages, which calls for detailed characterization of the thermochemistry of each reaction step. Experiments based on a combination of thermoanalytical and calorimetric techniques indicate that mild chemisorption at low temperature is moderately exothermic. Reactions occurring as preoxidized carbon is exposed at higher temperatures are also overall exothermic. This is consistent with a mechanism that assumes that oxygen is uptaken in a metastable form at moderate temperature, and that metastable surface oxides may be stabilized at higher temperatures into more energetically favourable carbon-oxygen complexes. Stable surface oxides are eventually desorbed at high temperature into CO and CO<sub>2</sub>.

A simple model of the CarboLoop process has been developed, based on simplified material and energy balances on the oxidizer and the desorber. Model computations have been performed to determine key process variables, like the solid recirculation rate, the carbon loading in both reactors, the thermal throughput at the oxidizer and at the desorber.

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