PERFORMANCE OF A DUAL FLUIDIZED BED REACTOR FOR CHEMICAL LOOPING COMBUSTION WITH OXYGEN UNCOUPLING

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Abstract – Chemical looping with oxygen uncoupling (CLOU) is a variant of chemical looping combustion which uses as fluidized bed particles specific solid oxygen carriers which readily liberate gaseous oxygen (O_2) in the fuel reactor. This enables much more efficient combustion of solid fuels such as coal than conventional chemical looping combustion, which relies on *in situ* gasification of char in to produce syngas that can react heterogeneously with the solid oxygen carrier.

The CLOU process for coal is an especially interesting application of fluidized bed technology since several types of reactions take place within the reactors. For copper-based oxygen carrier particles, the copper cycles between cuprous and cupric oxide ($Cu_2O + ½ O_2 \leftrightarrow 2 CuO$). Volatiles released from coal during pyrolysis may react with oxidized copper or with released oxygen gas. Char reacts primarily with released oxygen. Balancing oxygen supply to the fuel reactor, heat generation and temperatures and global and internal circulation rates is a challenge.

The University of Utah has been researching CLOU technology for 10 years, studying fundamental reaction kinetics for copper-based CLOU oxygen carriers, performing lab- and bench-scale experiments in single and dual fluidized beds, and developing reactor models through computational fluid dynamic modeling using Barracuda VR™. Recently the university began testing a 200 kW_{th} dual circulating fluidized bed process development unit (PDU) for processing coal. The design process for that reactor, reactor simulations, operational experience and practical challenges of the PDU system are presented.

INTRODUCTION

Chemical looping combustion (CLC) is an indirect combustion technology with inherent CO_2 capture that involves circulation of metal-based "oxygen carrier" bed particles between two fluidized bed reactors. In the so-called air reactor, which is fluidized with air, the metal is oxidized. The oxygen carrier particles are separated in e.g. a cyclone and transferred via a loop seal to a second reactor, the so-called fuel reactor, which is typically fluidized with steam or recycled CO_2. Fuel fed to the fuel reactor reacts with oxygen from the oxidized metal, thus achieving indirect combustion while reducing the oxygen carrier, which is then returned to the air reactor complheting the cycle. Because nitrogen is not introduced into the fuel reactor, the effluent gas is nearly pure CO_2 after water vapor has been condensed by cooling.

Chemical looping with oxygen uncoupling (CLOU) is a variant of CLC technology that involves use of oxygen carriers containing specific metals and associated oxides to spontaneously release ("uncouple") oxygen as gaseous O_2 in the fuel reactor. This is possible because in the air reactor, the high O_2 partial pressure favors the oxidized metal but in the high temperature, low-O_2 conditions of the fuel reactor, the equilibrium behavior of the carrier oxidation/reduction reaction favors gaseous O_2. The advantage of CLOU over conventional chemical looping combustion of solid fuels, which relies on *in situ* gasification and heterogeneous combustion of the resulting syngas by a non-CLOU carrier such as ilmenite, is the much faster char conversion that is achieved by reaction with O_2 versus gasification with H_2O and CO_2.

Only a few metal complexes that exhibit CLOU behavior in the range of chemical looping combustion temperatures have been identified. Copper is one such metal and is attractive due its fast reaction rates and because it is thermodynamically favored to completely convert gaseous hydrocarbons to CO_2 and H_2O (Garcia-Labiano et al., 2004). When used as a CLOU carrier, copper cycles between the Cu^{+2} cupric (CuO) and Cu^{+1} cuprous (Cu_2O) states:

$$Cu_2O + ½ O_2 \leftrightarrow 2 CuO \quad (1)$$

In addition, because of the low heat of reaction, Cu_2O/CuO looping is overall exothermic in both the air reactor and fuel reactor, whereas other materials are exothermic in the air reactor, but would require heat input to the fuel reactor since the heat required to reduce the carrier exceeds that given off by the fuel as it combusts (De Diego et al., 2007).

The equilibrium curve for Reaction 1 above is shown in Fig. 1. At temperatures above approximately 800°C, in otherwise low-O_2 environments (such as the fuel reactor of a chemical looping system), the reverse reaction takes place, generating O_2. If the O_2 continues to be consumed (e.g., by reaction with fuel), the CuO decomposition reaction will continue to progress. It has been shown that conversion of petcoke by CLOU is as much as 50 times faster than conversion by conventional CLC with an iron-based carrier, which requires in-situ conversion of petcoke to syngas by relatively slow gasification reactions (Mattisson et al., 2009).

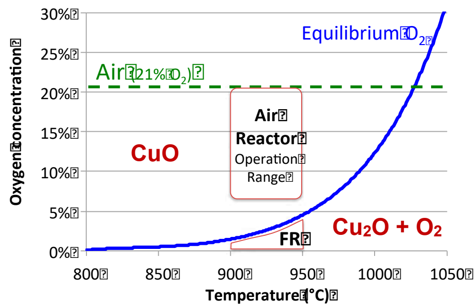


Fig. 1. CuO/Cu_2O equilibrium diagram showing the range of operating conditions for CLOU air and fuel reactors.

The University of Utah has been researching CLOU for nearly 10 years. Development and scale-up of the process has involved detailed analysis of fundamental reaction kinetics for copper-based CLOU oxygen carriers, lab- and bench-scale experiments in single and dual fluidized beds, process modeling and computational fluid dynamic modeling using Barracuda VR™. Recently the university began testing a 200 kW_{th} dual circulating fluidized bed process development unit (PDU) designed specifically for processing coal by copper-based CLOU. This paper describes the design of the dual fluidized bed reactor system, performance of copper-based chemical looping with oxygen uncoupling in terms of CO_2 capture and coal conversion, and operating experience with the PDU to date.

CLOU REACTOR DESIGN

The CLOU process for coal is an especially interesting application of fluidized bed technology since several types of reactions take place within the reactors. The oxygen carrier bed particles are reactive and undergo repeated oxidation and reduction (e.g. reaction 1). Volatiles released from coal during pyrolysis may react with solid oxidized copper (CuO or Cu_2O) or with gaseous O_2 released in the fuel reactor. Char reacts primarily with released O_2. Balancing (1) oxygen supply and distribution in the fuel reactor, (2) heat generation and associated local temperatures, and (3) global and internal circulation rates presents a good engineering challenge. Designing a large-scale CLOU reactor system involves specifying details such as those included in Fig. 2.

Air reactor	**Fuel reactor**	**Oxygen carrier**
– Type (bubbling, circulating, etc.)	– Type (bubbling, circulating, etc.)	– Metal (CuO) wt% loading
– Target temperature	– Target temperature	– Circulation rate
– Size (volume)	– Size (volume)	– Particle size
– Oxygen carrier residence time distribution	– Oxygen carrier residence time distribution	**Fuel feeding**
– Incoming air flow rate	– Fluidization gas (steam, CO_2, mixture)	– Fuel feed rate
– Target outlet oxygen concentration	– Fluidization gas preheat requirements	– Fuel feed location
– Air residence time	– Cooling duty and cooling system design	– Fuel particle size
– Air preheat requirements		**Other**
– Cooling duty and cooling system design		– Carbon stripper requirements and design
		– Gas-solid separation system design
		– Loop seal design and arrangement

Fig. 2. Factors to consider in design of a dual fluidized bed CLOU system.

Reaction fundamentals

To properly design a CLOU system, it is desirable to have as much information as possible about the underlying processes associated with oxidation and reduction of the oxygen carrier as well as conversion of the coal. Significant research on devolatilization and combustion of coal has been performed and published relationships and predictive models are readily available. Behavior of oxygen uptake and release from copper-based oxygen carrier is less well studied. It is valuable to understand the intrinsic chemical kinetics of both the forward (oxidation) and reverse (reduction) reactions shown in reaction (1). Ideally, it is useful to have rate expressions applicable across a broad range of conditions, for example of the form below for cuprous oxide oxidation:

$$rate = A\exp\left(\frac{-E_a}{RT}\right)\left[\mathrm{Cu_2O}\right]^{\alpha}\left[\mathrm{O_2}\right]^{\beta} \tag{2}$$

where A is a pre-exponential constant, E_a is the activation energy and α and β are reaction orders.

Interestingly, the thermodynamic behavior shown in Fig. 1 affects the rate of the carrier oxidation and decomposition (uncoupling) reactions. It is well understood that rates of reversible reactions such as reaction (1) are a affected by the difference between the actual and equilibrium concentrations of reacting species. This has also been observed to occur with copper-based oxygen carriers operating in the CLOU regime (Gayan et al., 2012). This makes identification of intrinsic kinetics of the respective oxidation and reduction reactions challenging. For example, several groups studying CLOU have reported a decrease in the rate of oxidation by air at higher temperatures (Eyring et al., 2010; Brandt et al., 2011; Gayan et al., 2012), which is due primarily to a decrease in the difference between the equilibrium O_2 partial pressure and air's partial pressure of 0.21 atm. Similarly, in certain types of experiments the rate of cupric oxide reduction to release O_2 is affected by that released O_2.

To University of Utah has undertaken several studies to investigate and develop rate models for Cu_2O oxidation and CuO uncoupling/O_2 generation as functions of local environment and oxygen carrier properties. These results have been published (Sahir et al., 2011; Sahir et al., 2012; Clayton et al., 2014a; Clayton and Whitty, 2014b), and other groups have also reported on reaction behavior of copper-based oxygen carriers for CLOU reactors.

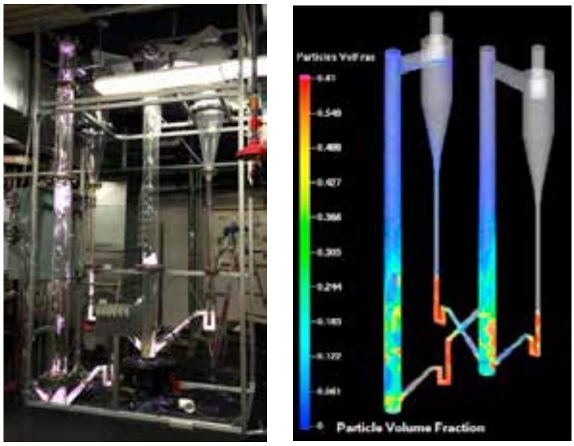
In addition to chemistry associated with oxidation and reduction/oxygen release of the solid carrier materials, reaction analysis must consider rates and product distribution of devolatilization of the coal, heterogeneous combustion and gasification kinetics of coal char and gas-phase reactions. Properly accounting for these reactions and heats associated with the reactions is necessary to properly model a CLOU-based coal chemical looping system.

Reactor modeling

A driver of the chemical looping research at the University of Utah is to develop CLOU technology to semi-pilot scale through a combination of reactor operation and modeling. Initial reactor models were relatively simple Excel-based mass and energy balance-type models that used published correlations for oxygen carrier circulation rates and gave relatively cursory consideration to reaction kinetics and reactions other than oxygen carrier oxidation and reduction and coal char conversion. This was sufficient for preliminary design of the university's 200 kW dual circulating fluidized bed CLC/CLOU process development unit.

Since 2013 the University of Utah has used CPFD's Barracuda VR® computational fluid dynamic modeling software package to help design and simulate performance of chemical looping reactors. Complexity and representativeness of the Barracuda models has increased with time as improvements have been made to particle characterization and size distribution, chemical reactions and rates, heat generation and transfer, and submodels for particle-gas interactions. The Barracuda models are now quite robust and simulations of the 200 kW PDU have been valuable for specifying operating conditions and for interpretation of performance as the system has gone through the startup phase.

To help understand behavior of the 200 kW PDU and as a tool for validation of the Barracuda VR® models, an acrylic cold flow model of the PDU was constructed (Fig. 3a). The cold flow model was designed in accordance with Glicksman's scaling relationships and is approximately 60% the size of the full-scale system. The cold flow system has over 20 pressure measurement transmitters and a method for measuring the solids circulation rate. The system is useful not only for visualization of what takes place within the dual bed PDU, but as a source of data for validation of hydrodynamics in the Barracuda simulations (Fig. 3b).



(a) (b)

Fig. 3. (a): Cold flow model of the 200 kW PDU and (b) Barracuda simulation of the cold flow model showing particle volume fraction.

Reactor construction

The CLC reactor design has combined fundamental understanding of oxygen carrier and coal conversion behavior, experience operating fluidized bed reactors at various scales and computational models and reactor simulations. Two scales and designs of reactor systems have been built.

10 kW dual bubbling bed bench-scale reactor. A bench-scale dual bubbling fluidized bed chemical looping system with a capacity of roughly 10 kW or roughly 1.5 kg/h coal feed (Fig. 4) was built to study CLOU behavior at a scale more manageable and flexible than the PDU. The system was constructed by modifying an existing 10 cm diameter electrically heated steam-fluidized gasifier to serve as the fuel reactor, incorporating an overflow pipe that carries particles through a loop seal into an air reactor. The air reactor is a 15 cm diameter fluidized bed that operates as a bubbling bed with a cone at the top to reduce the diameter to 3.7 cm so that the velocity increases to transport particles through a riser into a cyclone. Particles flow from the cyclone through a dipleg and loop seal back to the bottom of the fuel reactor. Coal is fed through a twin auger feeder into the bottom of the fuel reactor diametrically opposite the inlet of recycled particles. The 10 kW system is used for scoping studies, to investigate carbon conversion and char properties, and to expose candidate oxygen carrier materials to actual chemical looping conditions for extended lengths of time.

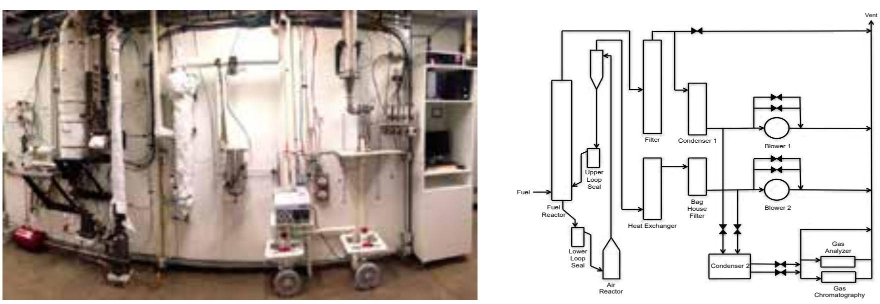


Fig. 4. Photograph and schematic of UofU 10 kW bench-scale chemical looping system.

200 kW chemical looping process development unit (PDU). The University of Utah recently completed construction of a process development unit for CLC and CLOU. The subsystems are sized for a thermal input of roughly 240 kW and based on models of expected performance the unit should be able to comfortably handle operation at 200 kW in CLOU mode. Initial tests will target operation at lower load, closer to 100 kW.

The 200 kW system represents a significant scale-up of CLOU technology, and several decisions regarding design had to be made. In addition to determining reactor characteristics tabulated earlier, it was necessary to decide whether the reactor should be made of metal and electrically heated or whether it should be refractory lined and preheated. Chalmers University of Technology operates an electrically heated 100 kW chemical looping reactor (Markström et al., 2012). That represents an upper limit of what can practically be electrically heated. The University of Utah operates several other pilot-scale systems at its Industrial Combustion and Gasification Research Facility (ICGRF) and all of those systems are refractory-lined. Based on good experience with those pilot systems and concern over durability of materials at combustion temperatures, it was decided to make the CLC PDU a refractory lined system.

Both the air and fuel reactors are circulating fluidized beds. Again, part of the rationale behind that decision was familiarity with operating a similarly-sized circulating fluidized bed combustor, which has been at the ICGRF for over 20 years. Also, CFBs are considered more scalable to industrial scale than bubbling fluidized beds. To help separate control of the two reactors, the fuel reactor recycles material from the cyclone back to the fuel reactor bed, but all material from the air reactor flows through the cyclone into the fuel reactor. A dedicated connection transports particles from the fuel to the air reactor via a loop seal. The resulting configuration of the two beds is shown in Fig. 5 and a photograph of the completed system is presented in Fig. 6.

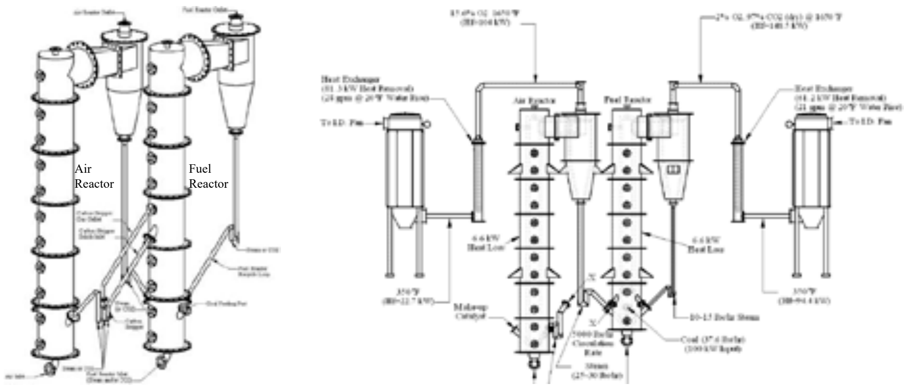


Fig. 5. Reactor arrangement and configuration of the 200 kW CLC PDU.

Fig. 6. Photograph of the University of Utah chemical looping combustion PDU.

The PDU was built without a carbon stripper to burn out char that is undesirably transferred to the air reactor. The CLOU process has been demonstrated to achieve much better carbon conversion than conventional CLC of coal with e.g. ilmenite, so the need for a carbon stripper should be less. Nonetheless, incorporation of a carbon stripper will undoubtedly help conversion, even for a CLOU system. It has been decided to operate first without one so that the quantity and nature of char carried to the air reactor can be characterized to help design an appropriate carbon stripper.

PERFORMANCE OF DUAL BED CLC PDU

Performance of the PDU system in terms of hydrodynamic performance, carbon capture efficiency and coal conversion is being evaluated through a combination of reactor operation and computational simulation.

Operating Experience

Construction of the 200 kW PDU was completed fall of 2016 and the system has been undergoing shakedown testing since that time, initially starting with cold tests of fluidization and particle circulation rate. The bed material does fluidize and is transported as expected, demonstrating good circulation both within the fuel reactor with particles from the fuel reactor cyclone returned to the reactor, as well as between the reactors with particles from the air reactor cyclone transferred to the fuel reactor. In order to transfer oxygen required for combustion from the air reactor to the fuel reactor, it is important to have good circulation of oxygen carrier. For operation at 100 kW thermal input with an oxygen carrier containing 20% CuO, a circulation rate of approximately 2600 kg/h is required. Testing so far has been conducted using ilmenite with an average particle size of roughly 120 microns. Measured performance indicates that circulation rate depends strongly on the system bed inventory and air reactor gas flow rate, and that circulation well in excess of that required is achievable (Fig. 7).

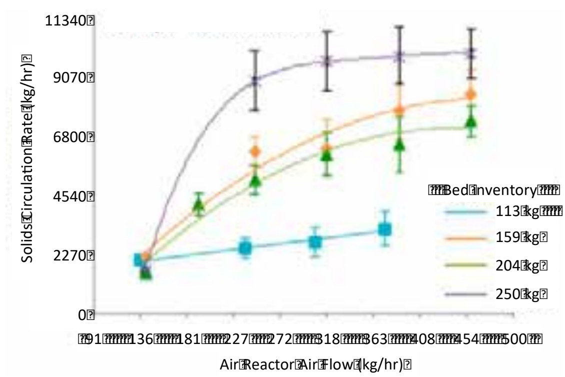


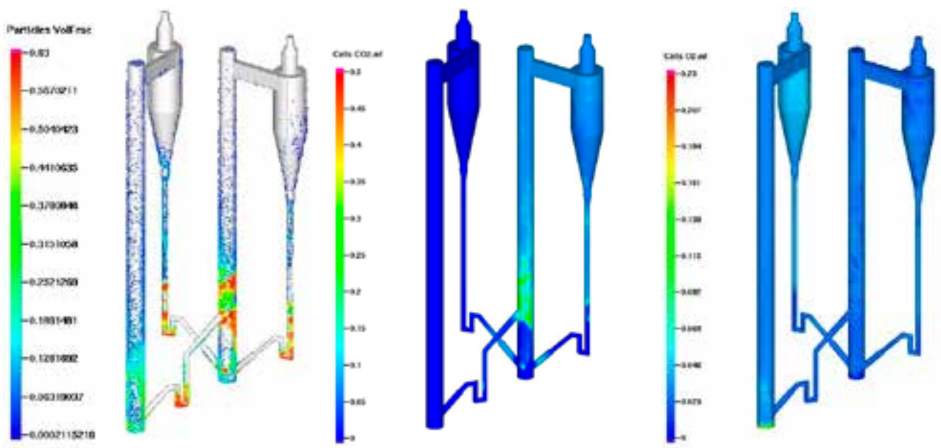
Fig. 7. Ilmenite circulation rates in PDU, measured at approx. 600°C.

A practical operational challenge has been material loss through the cyclones. In extreme cases, during longer operation as much as one-third of the bed material has been lost in a 24-hour period. The material loss did not occur at a steady rate, but instead there appeared to be upsets that resulted in much loss. A thorough analysis of the system design as well as a systematic series of tests was performed to help identify the cause of the material loss. Three factors were identified as contributing to the material loss: (1) the particle size of the delivered ilmenite was lower than expected, (2) the cyclone was misdesigned and had a barrel diameter about twice that required for efficient particle separation, and (3) occasionally fluidization of the loop seals would cease, resulting in buildup of particles in the downcomers from the cyclones. To address the material loss, smaller cyclones of stainless steel were constructed and installed inside the original refractory cyclones and loop seal operation was improved to ensure fluidization was maintained. This reduced material loss to less than 4% over a 24-hour period. Future operation will use larger particle sizes, which is expected to further reduce bed loss.

Reactor Simulation

Simulations of operation in the PDU when operating on coal have been developed using Barracuda VR™. Earlier investigations into sensitivity of simulated performance and the assumed reaction mechanism for coal char revealed that considering char combustion as a two-stage process with carbon monoxide as an intermediate is necessary to avoid having unrealistically high particle temperatures. Results of a typical simulation operating the system at 100 kW_{th} are shown in Fig. 8. The simulation includes local rates of oxygen carrier oxidation and reduction (O_2 release) as well as rates and yields associated with coal devolatilization, char oxidation rates for the local environment, gas-phase reactions and heat generation and transfer. The simulations indicate that conversion in the system is efficient, with very little CO_2 exiting the system through the air reactor due to carryover of coal char from the fuel reactor.

The simulations are useful for providing guidance on operating conditions. One of the key operational questions regards the optimum size of coal particle to feed to the system. Very fine particles risk being carried out of the reactor before being completely converted and require more energy to produce by grinding. Large particles, on the other hand, risk being carried into the air reactor before being completely converted, with the consequence that CO_2 from combustion in the air reactor is not captured. The simulation models are also being used to gauge whether a carbon stripper will be necessary to completely burn out the carbon. As the PDU is brought online, data from that system will be used to validate the simulations and to improve them for future designs.



(a) (b) (c)

Fig. 8. Simulation of performance of CLOU PDU when processing coal. Figures show (a) particle volume fraction; (b) CO_2 concentration and (c) O_2 concentration. The air reactor is on the left, fuel reactor is on the right. Coal is fed into the bottom of the fuel reactor. Bed mass: 155 kg. Air reactor flow: 256 kg/h. Fuel reactor (steam) flow: 154 kg/h. T: 900°C.

CONCLUSIONS

Chemical looping with oxygen uncoupling in a dual fluidized bed reactor offers an efficient method for processing solid fuels that are otherwise challenging to convert using conventional oxygen carriers. Processing of coal through CLOU is an interesting application of fluidized bed technology, since there are multiple types of reactions taking place simultaneously, particularly in the fuel reactor where gaseous oxygen is released from the carrier material, coal is devolatilized, volatiles react either with gaseous oxygen released from the carrier or with the oxidized carrier metal, coal char is combusted by released oxygen and gas-phase reactions may take place. The technology has been developed to a point where small pilot-scale process development units are being brought online, and the vanguard of reactor simulations involve not only hydrodynamics of the system but also incorporate reactions of the oxygen carrier, coal volatiles and coal char. Operation of a dual bed process development unit at the University of Utah has so far gone well, although full processing with coal has not yet been achieved. The bed material does flow as desired, circulation rate can be controlled within a given window primarily through adjustment of the air reactor air flow rate and the circulation rate is more than sufficient to provide oxygen for 200 kW of coal feed. Simulations suggest that operation will be successful, and future tests will examine performance as a function of operating conditions and fuel properties.

NOTATION

A	pre-exponential rate constant	T	temperature, K
E_a	activation energy, kJ/mol	α, β	reaction order
R	ideal gas law constant		

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