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Integration of Multiphase CFD Models With Detailed Kinetics to Understand the Behavior of Oxygen Carriers Under Pressurized Conditions

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ABSTRACT

The Power Sector is undergoing a rapid technological change with respect to implementation of low carbon technologies. The IEA Energy Outlook 2017 shows that the investments in Renewables for the first time are equal to those on the fossil sources. It is likely that the conventional gas turbines and internal combustion engines will need to be integrated in systems employing biofuels and/or CCUS (Carbon Capture Usage and Storage). Also, the European Union is moving rapidly towards low carbon technologies (i.e. Energy Efficiency, Smart Grids, Renewables and CCUS), see the Energy Union Strategy. This paper presents the basic for the design of CLC combustors to be coupled with gas turbines. Based on CFD modeling and detailed kinetics models.

Keywords: Chemical Looping Combustion, Bioenergy, Carbon Capture and Storage, Computational Fluid Dynamic, Gas Turbines

NONMENCLATURE

Abbreviations	
CFD	Computational Fluid Dynamic
CLC	*Chemical Looping Combustion*
GT	*Gas Turbine*
OC	*Oxygen Carrier*

1. CFD MODELING OF FLUIDISED BED COMBUSTION

The Power Sector is undergoing a rapid technological change with respect to implementation of low carbon technologies. The IEA Energy Outlook 2017 shows that the investments in Renewables for the first time are equal to those on the fossil sources. It is likely that the conventional gas turbines and internal combustion engines will need to be integrated in systems employing biofuels and/or CCUS (Carbon Capture Usage and Storage). Also, the European Union is moving rapidly towards low carbon technologies (i.e. Energy Efficiency, Smart Grids, Renewables and CCUS), see the Energy Union Strategy.

In this context a Marie Curie project has been funded in the Spanish National Research Council (CSIC), Instituto de Carboquimica (ICB) named GTCLC-NEG which objective is to promote a Carbon Negative Technology, able to burn multiple biofuels derived from biomass (eg, pyrolysis oil, biogas and syngas) and to capture the CO_2 emissions at a very low cost. In this way there will be negative GHG emissions due to the use of BECCS (Bioenergy with Carbon Capture and Storage), a technology which is going to be developed within 2050, according to the IPCC. The proposed plant is based on the coupling of a Chemical Looping Combustor to a gas turbine, as proposed in figure 1.

As it can be seen in the proposed plant the compressed air used to oxidize the oxygen carrier is then expanded in a gas turbine to produce electricity. In the

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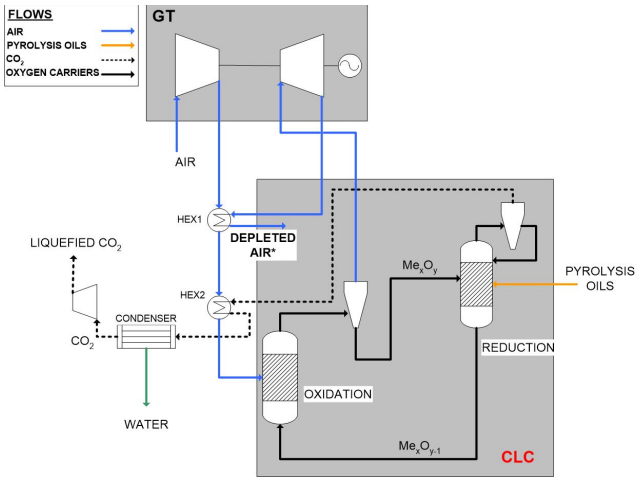

Fig. 1. GTCLC-NEG LAYOUT

fuel reaction biofuels (in this case pyrolysis oils) are used to reduce the oxygen carrier. Possible technical barriers are: (1) high efficiency bimetallic oxygen carriers are needed; (2) low attrition rate oxygen carriers are needed which can work in extreme conditions; (3) kinetics aspects under high pressure and temperature conditions are not known; (4) reactor injection system has to be adapted to biofuels; the use of the hot air produced from the air reactor (see figure 1) in a gas turbine has to be optimized; exhausts should be filtered to retain the dust released by oxygen carrier attrition; (5) high electrical efficiency of the power system has to be granted together with high fuel conversion in the combustor [1,2,3].

To summarize, one of the most critical aspects of the technology is the operation of the chemical looping combustor at high pressures. This has been rarely done on the large scale, for this reason the modeling of the reactor and of the chemical processes that happen during pressurized chemical looping combustion appears to be of scientific interest.

Effective models have been already developed at 0D level in the Instituto de Carboquimica [4], these are based on the Shrinking Core Model (SCM) which is widely adopted in literature to describe the oxygen carrier behavior. Also CFD models have been developed by [5-28] Nevertheless, the effect of pressure on CLC process has not yet been fully described.

This paper aims at presenting different strategies which can be found in the literature, to model the fuel and the air reactors with CFD software with improved kinetic constants. In the literature there are about 150 papers on CFD at the moment (27th august 2021). The main research groups are cited together with the representative work in table 1.

Table 1: Most significant works on CFD modeling of Chemical Looping Combustion, Gasification and Reforming

Group	Source	Software	DEM
Leeds Uni, IFP Energies Nouvelles and Total	[5]	ANSYS FLUENT™ and EDEM	Yes
Singapore NUS	[6]	N.R.	No
HUST, China	[7]	CPFD	No
Nanjing	[8]	ANSYS FLUENT™	No
SINTEF	[9]	PFC3D	Yes
Washington University	[10]	ANSYS FLUENT™	Yes
Masdar Institute of Science and Technology	[11]	ANSYS FLUENT™	No
TU Darmstadt	[12]	ANSYS FLUENT™	No
Imperial College	[13]	ANSYS FLUENT™	No
NETL	[14]	Barracuda	No
University of New South Wales	[15]	ANSYS FLUENT™	No
Harriot Watt University	[16]	MFIX	No
CPFD Software	[17]	Barracuda-VR™	No
Indian Institute of Technology	[18]	ANSYS FLUENT™	No
The University of Nottingham	[19]	ANSYS FLUENT™	No
The University of Newcastle (Australia)	[20]	ANSYS FLUENT™	Yes
Harbin Institute of Technology	[21]	K-FIX	No
Zhejiang University	[22]	MFIX	No
University of Utah	[23]	Barracuda-VR™	No
IMFT Tolouse, TU Wien	[24]	NEPTUNE_CFD	No
The University of Western Ontario	[25]	Barracuda-VR™	No
KAIST	[26]	ANSYS FLUENT™	No
University of North Dakota	[27]	MFIX	No

From table 1 it can be see that the most of the CFD studies are realized with ANSYS FLUENT™, nevertheless two interesting alternatives appear to be: the use of MFIX (Multiphase Flow with Interphase eXchange) software [28,29] developed at the National Energy Technology Laboratory (NETL) and available on the internet at http://www.mfix.org and the use of Barracuda-VR. Another important aspect is that the use of Discrete Element Models (DEM) is not much diffused at the moment. An interesting approach could be to join CFD-DEM analysis with detailed kinetics derived from TGA and controlled with molecular dynamics and DFT techniques.

2. DETAILED KINETIC MODELS OF IRON REDUCTION

If we consider the models presented in table 1, we see that very few of them (about 10%) consider chemical reactions. Among them few consider reduction of CH_4 with iron oxygen carriers, while Nickel oxides are regarded as the preferred oxygen carriers (OCs).

For this reason, in the MSCA project GTCLC-NEG it has been chosen to work at first with iron-based OCs which can be based on alumina loaded with iron, see [30], which grant a lower total solids inventory if compared with other iron-based OCs.

If we think at the iron reduction reactions which happen in the reactor, in [31] it is reported that during iron (hematite) reduction inside the reactor namely magnetite is generated with small concentrations of wustite; according to the following two equations:

$$12Fe_2O_3 + CH_4 \rightarrow 8Fe_3O_4 + 2H_2O + CO_2 \quad (1)$$

$$4Fe_3O_4 + CH_4 \rightarrow 12FeO + 2H_2O + CO_2 \quad (2)$$

The set of kinetic constants (activation energy, order of reaction and pre-exponential factor) for these two heterogeneous reactions have been calculated by several researchers (see [30]). These values can change depending on the diameter of the oxygen carriers, their purity and chemical characteristics and even the reaction conditions can have an influence. The kinetic triplets depend also by the model which is chosen for example in [32] it is chosen a modified volumetric model while more often a shrinking core model (SCM) is preferred, see [33]. If we take into consideration the values reported in [34] we can infer that for Tierga ore reduction (representing equation 1) with natural gas the following triplet can be considered:

- n (-) = 1.0 ± 0.05;
- $k_{s,0}$ ($mol^{1-n} m^{3n-2s-1}$) = $7.41 \cdot 10^5$
- Ech (kJ/mol) = 257 ± 14.

If we want to consider the second reduction equation (equation 2), we have to consider that Shi et al. 2008 [34] suggest that the kinetic constant (k) of the reaction between magnetite and wustite is the same of the kinetic constant of the reaction between hematite and magnetite.

If we want to couple a CLC combustor with a gas turbine, we have to take into consideration that for the aims of the GTCLC_NEG process the kinetic triplets need to be derived at high pressure (with Pressurized TGA tests, see table 2).

Table 2: PTGA tests on oxygen carriers

Group	Fuel	OC	Source
CSIC, Spain	Syngas	CuO/Al_2O_3, Fe_2O_3/Al_2O_3, NiO/Al_2O_3	[35-36]
USDOE	Syngas	NiO	[37]
Southeast University	CO, Coal	Hematite	[38-41]
The Ohio State University	CH_4, H_2	Fe_2TiO_5	[42,43]
Eindhoven University of Technology	CO, H_2	CuO/Al_2O_3 $NiO/CaAl_2O_4$	[44,45]
Canmet ENERGY & North China Electric Power University	CO	$FeTiO_3$	[46-48]
University of Kentucky	Coal char	$FeTiO_3$, Red mod	[49]
University of Science and Technology Beijing	CH_4	Cu-based	[50]
Korea Institute of Energy Research	CH_4	NiO, Mn_3O_4, CuO, Fe_2O_3	[51]
University of Connecticut	CH_4	Ni & Cu OCs	[52]
Ningxia University	Coal	Fe_2O_3/Al_2O_3	[53]

Pressurized Chemical Looping is well described in the recent review [54], many works presented in table 2 are

taken from it. Table 2 reports only reduction tests performed at high pressure, while CSIC and TU Eindhoven and also CanmetEnergy have realized also oxidation tests in pressurized conditions [55,56].

3. CONCLUSIONS

A state of the art on CFD modeling of CLC plants is proposed together with some reflections on the optimal kinetics to adopt for iron derived OCs on both atmospheric and pressurized conditions. It can be seen from the publication that pressurized CLC is rapidly gaining interest in the scientific community which is developing integrated approaches on the analysis of chemical and physical phenomena also based on modern DFT and MD modeling.

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