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# LIBPF

## Case study Molten Carbonate Fuel Cell System

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## Introduction

LIBPF (**LIB**rary for **P**rocess **F**lowsheeting) is a modelling tool to rapidly prototype and deploy small-footprint custom applications implementing computations for training, process engineer support, on-line process diagnostic, and data reconciliation. For more information regarding **LIBPF**, please see the website <http://www.libpf.com>.

The purpose of the **Molten Carbonate Fuel Cell System LIBPF demo** is to illustrate the process flowsheet solving capabilities of LIBPF, plus the front-end (User Interface), database repository and calculation server, based on a simplified steady-state model of a Molten Carbonate Fuel Cell (MCFC) plant similar to the one described in (1). The prototype shows basic functionality, but it could be easily extended to become a tool for off-line process diagnostic and reconciliation.

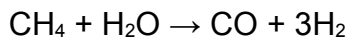
## Problem description

### *Feedstock and pretreatment*

Sugar cane residues are processed to a gas with an attractive Low Heating Value (LHV) containing CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O which after clean-up is fed to the plant of interest.

Said fuel enters the REFORMER after it has been warmed in a cross-flux heat exchanger (REGHEX) using hot gases coming from the same reformer.

Fuel preheating is necessary because of the endothermic reforming reaction:

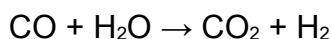


which is favoured by high temperatures, and, when is under way, subtracts heat and tends to lower the reactor temperature.

In the model this reaction has been assumed at thermodynamic equilibrium.

Through the reforming reaction CH<sub>4</sub>, which is still present in the feeding stream, is transformed into CO and H<sub>2</sub>, useful gases to feed MCFC stack.

Moreover the shift reaction:





also takes place in the reformer, giving  $H_2$  and  $CO_2$  and so enriching the biogas further. This reaction also has been considered at thermodynamic equilibrium in the model.

Reformed fuel comes out from the reformer hot and exchanges heat with the feeding stream in the heat exchanger; then it enters the anodic side of the stack.

In particular, as the stack inlet stream temperature is an important key for a proper MCFC operation; the heat exchanger area has been set in such a way to guarantee a suitable anodic inlet temperature of  $600\text{ }^\circ\text{C}$ .

The cathodic side on the other hand is fed with air that, before entering the electrode, is mixed with the cathodic exhaust gas in the mixer AIRMIX.

### Flowsheet

The process flowsheet is portrayed in figure 1.

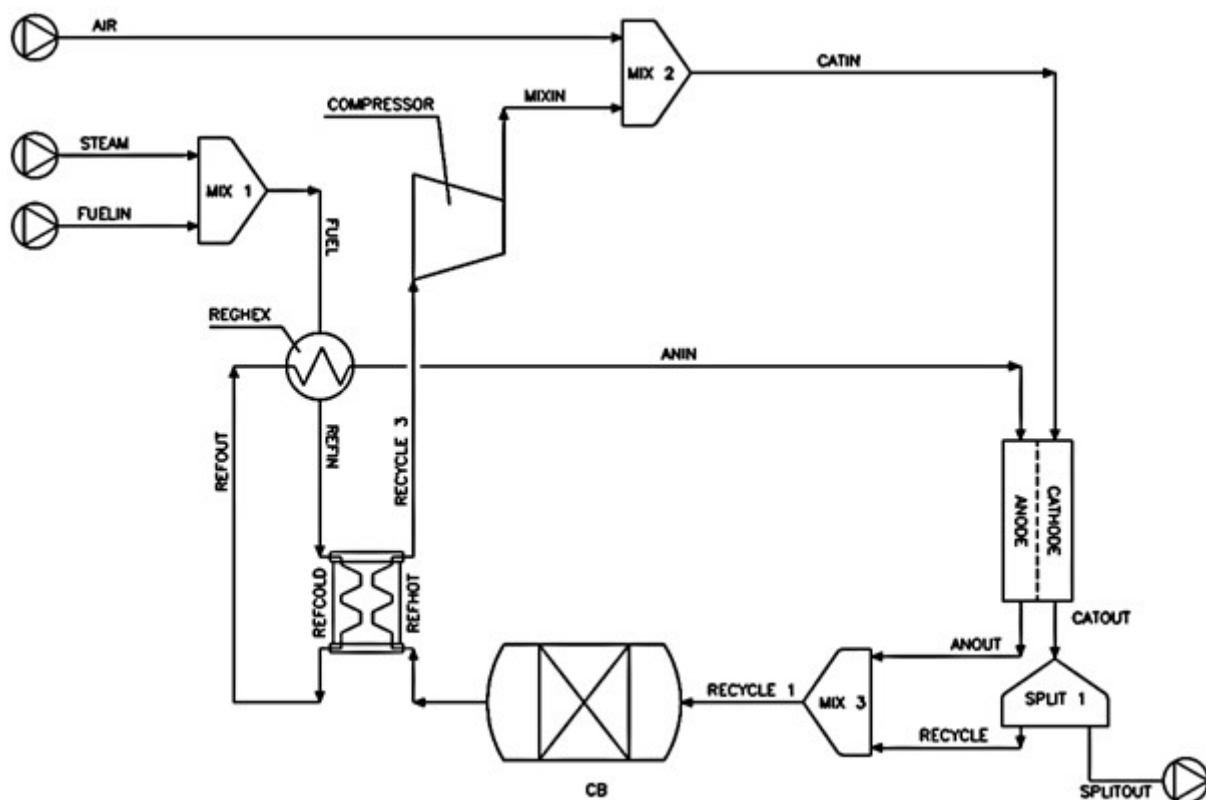


Figure 1 – Process Flowsheet



## ***Fuel cell***

The MCFC stack produces a direct electrical current by means of the electrochemical processes that take place inside it.

MCFCs are usually planar cells formed by a matrix (tile) filled with Li and K carbonates and coupled with two electrodes where the following electrochemical reactions occur:

- anode:  $\text{CO}_3^{2-} + \text{H}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2 \text{e}^-$
- cathode:  $\text{CO}_2 + \frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$
- overall reaction:  $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$

The fuel and the oxidant are fed separately, and the tile prevents gas crossover and guarantees an adequate ionic conduction and electronic insulation.

The stack is composed of a number of superimposed cells connected in series, via bipolar plates, to supply the requested voltage.

The MCFC stack has been modelled with a concentrated parameters electrochemical model based on (3).

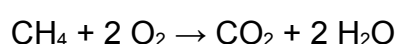
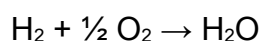
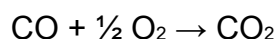
## ***Postprocessing and recycle***

The gaseous stream that is present at the anodic exit contains unreacted  $\text{H}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  coming from the electrochemical reaction in the anodic zone, little quantities of unreacted  $\text{CO}$  and  $\text{CH}_4$ , and  $\text{N}_2$ .

Instead, at the cathodic exit a gaseous stream containing unreacted  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$  is obtained.

This gaseous stream is partly (about 40%) released into the atmosphere (SPLITOUT), and partly channelled into the catalytic burner CB (RECYCLE) in which it is mixed with the anodic gaseous stream.

The stack exhausts mixed in this way react through the following complete oxidation reactions:





which, in the model, involve the total combustion of the unreacted anodic gases thanks to the cathodic  $O_2$ . These reactions are exothermic and so they generate heat, therefore, steam and  $CO_2$  created in the burner enter the reformer with the unreacted stack gases; here they exchange heat with the feeding stream and so the necessary heat for the reforming reaction is produced.

The gases leaving the reformer regain pressure in a blower and then they are mixed with the air that is fed to the cathodic size.

### **Main data**

The FUELIN stream is the biogas received from the clean-up section after the biomass gasifier, pressure 3.6 bar, temperature 400 °C, total mole flow 10 kmol/h and composition as follows:

Table 1  
Composition (mol%) and LHV ( $MJ/Nm^3$ ) of gas coming from gasifier

Gas coming from gasifier (mol%)	
CH <sub>4</sub>	4
CO	22
CO <sub>2</sub>	16
H <sub>2</sub>	46
H <sub>2</sub> O	12
LHV <sup>a</sup>	8.7

<sup>a</sup> In  $MJ/Nm^3$ .

The STEAM stream is saturated steam at 5 bar and is fed with an excess of 75% with respect the stoichiometric amount required for complete conversion of  $CH_4$  and  $CO$  to  $H_2$  (this results in a total humidified feed flow of 34.6 kmol/h in accordance with (1) page 51).

The AIRIN stream at 137 °C was set to 56.5 kmol/h in accordance with (1) page 52 to get a cathode inlet temperature of 600 °C.

The split ratio to SPLITOUT in SPLIT1 is set to 40%.



## Modelling Simplifications

In this case study the following model simplifications were used:

- 1) The compressor is isentropic with ideal yield  $\theta = 1.0$
- 2) All the units are modelled as concentrated parameters

## Problem translation in LIBPF

### Input

The problem is specified in LIBPF in four steps:

- 1) subclass a new class from `flowsheet` to represent the case

```
class mcfcsystem : public flowsheet<zero_zero> {
private:
    static string type_;
    void maketables(long);
public:
    mcfcsystem(const string &t, const string &d, modelBase *p);
    mcfcsystem(long cid);
    virtual void makeuserassembly(std::list<assignment *>::iterator &p);
    virtual void setup(void);
    virtual const std::string &type(void) const { return type_; }
}; // mcfcsystem
```

- 2) define case connectivity in `maketables` virtual method of new type

```
void mcfcsystem::maketables(long CID) {
    if (CID != -1) return;
    makeVertex<mixer> ("MIX1", "Mixes inlet air with recompressed reformer outlet");
    makeVertex<mixer> ("MIX2", "Mixes anode and cathode outlets");
    makeVertex<genflash11> ("BLOWER", "Compresses reformer outlet");
    makeVertex<hx> ("REGHEX", "Regenerative heat exchanger");
    makeVertex<splitter> ("SPLIT", "Cathode outlet splitter");
    makeVertex<hx> ("REFORMER", "Reformer",
        map_list_of<string, long>("nReactions", 2)
        ("nMultiReactions", 0),
        map_list_of<string, string>("embeddedTypeReactions[00]", "reactionCH4_Ref_Eq")
        ("embeddedTypeReactions[01]", "reactionWGS_Eq"));
    makeVertex<genflash11> ("CB", "Catalytic burner",
        map_list_of<string, long>("nReactions", 3),
        map_list_of<string, string>("embeddedTypeReactions[00]", "reactionCH4_TC")
        ("embeddedTypeReactions[01]", "reactionCO_TC")
        ("embeddedTypeReactions[02]", "reactionH2_TC"));
    makeVertex<multihx> ("FC", "MCFC stack",
        map_list_of< string, long>("nReactions", 1)
```



```

        ("nMultiReactions", 1)
        ("nStreams", 2),
    map_list_of<string, string>("embeddedTypeReactions[00]", "reactionWGS_Eq")
        ("embeddedTypeMultiReactions[00]", "multiReaction_MCFC")
);

makeEdge<streamV>("AIRIN", "Inlet fresh air", "source", "out", "MIX1", "in1");
makeEdge<streamV>("FUELIN", "Humidified fuel", "source", "out", "REGHEX",
"coldin");
makeEdge<streamV>("REFIN", "Preheated fuel", "REGHEX", "coldout", "REFORMER",
"in2");

makeEdge<streamV>("ANIN", "Reformed fuel to anode", "REGHEX", "hotout", "FC",
"in1");
makeEdge<streamV>("ANOUT", "Anode outlet", "FC", "out1", "MIX2", "in1");
makeEdge<streamV>("CATIN", "Cathode inlet", "MIX1", "out", "FC", "in2");
makeEdge<streamV>("CATOUT", "Cathode outlet", "FC", "out2", "SPLIT", "in");
makeEdge<streamVL> ("MIXIN", "Recompressed flues", "BLOWER", "out", "MIX1", "in2");
makeEdge<streamV>("REFOUT", "Reformed fuel", "REFORMER", "out2", "REGHEX",
"hotin");
makeEdge<streamV>("SPLITOUT", "Purged cathode out", "SPLIT", "out1", "sink", "in");
makeEdge<streamV>("RECYCLE", "Recycled cathode out", "SPLIT", "out2", "MIX2",
"in2");
makeEdge<streamV>("RECYCLE1", "Recycle to CB", "MIX2", "out", "CB", "in");
makeEdge<streamVL>("RECYCLE2", "CB outlet", "CB", "out", "REFORMER", "in1");
makeEdge<streamV>("RECYCLE3", "Recycle", "REFORMER", "out1", "BLOWER", "in");
} // mcfcsystem::maketables

```

3) set up model inputs in setup virtual method of new type

4) enter feedback specifications to be converged iteratively in makeuserassembly virtual method of new type

```

void mcfcsystem::makeuserassembly(std::list<assignment *>::iterator &p) {
    long int i(0);
    MakeAssignment(*0("FC:multiReactions[00]")->Q("z"),
        *0("FC:multiReactions[00]")->Q("z") *
        (0.75/(1.0-(*0("ANOUT:Tphase")->Q("ndotcomps", "H2")) + *0("ANOUT:Tphase")-
>Q("ndotcomps", "CO")))/(*0("ANIN:Tphase")->Q("ndotcomps", "H2")) + *0("ANIN:Tphase")-
>Q("ndotcomps", "CO"))),
        "Set fuel utilization");
} // mcfcsystem::makeuserassembly

```

## Flowsheet output

The connectivity is represented within LIBPF as the Directed Cyclic Graph shown in figure 2.

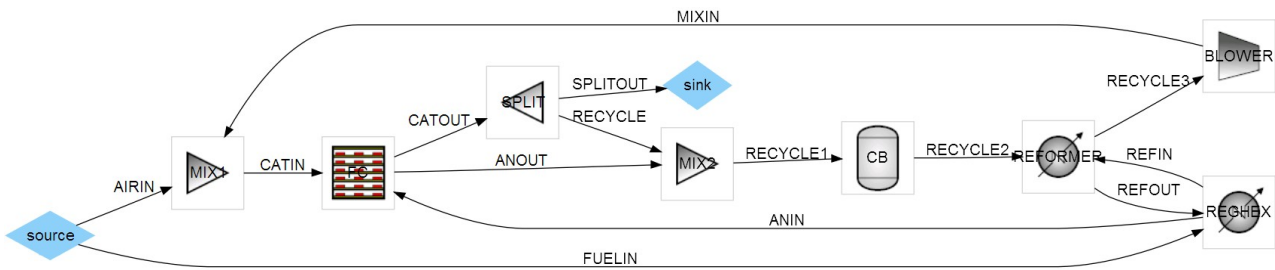


Figure 2 - Internal representation of flowsheet

## Resolution

The commands

```
addcut("REFOUT")
```

```
addcut("MIXIN")
```

in the setup method cut the stream REFOUT and MIXIN and make the graph a Directed Acyclic Graph shown in figure 3.

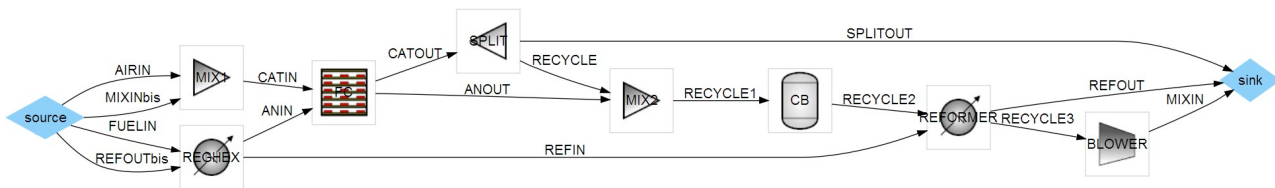
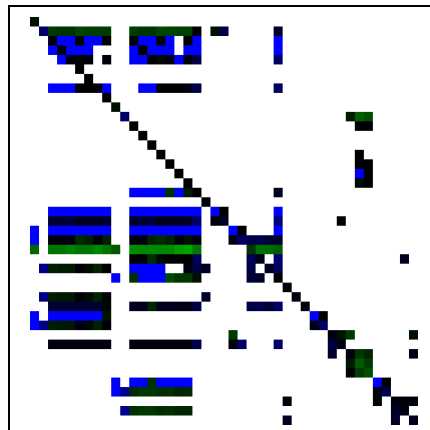


Figure 3 - Internal representation of flowsheet after cutting streams

The new streams REFOUTbis and MIXINbis become feedstreams, whose values are initialized appropriately in the setup method; the DAG can be then solved sequentially.

For maximum speed only two sequential iterations are performed, then the solution proceeds simultaneously.



*Figure 4 - Jacobian for simultaneous resolution*

For the simultaneous solver this problem exposes 54 unknowns, and gets solved in 3 iterations; the Jacobian is shown in figure 4, where the blue cells represent tiny elements; it has a filling of about 20 %. The timings in typical modern hardware are 3 s for the initial resolution and 2 s for the subsequent resolutions.

An extract of the results is shown in figure 4.

	A	B	C	D	G	J	M	P
1				AIRIN	STEAM	FUELIN	FUEL	REFIN
2				Inlet fresh air	Inlet water steam	Inlet gas from biomass gasifier	Humidified fuel	Preheated humidified fuel
3		Pressure	bar	3.600	5.000	3.600	3.600	3.600
4		Temperature	°C	137.0	151.8	450.0	241.7	383.6
5		Vapor molar fraction		1.000	1.000	1.000	1.000	1.000
6		Molecular weight	kg/kmol	28.8	18.0	16.9	17.7	17.7
7		Specific Heat	kcal/kg/°C	0.244	0.457	0.498	0.485	0.494
8		Specific Enthalpy	kcal/kg	27.195	-3143.905	-1482.681	-2684.819	-2615.554
9		Density	kg/m3	3.03	2.67	0.24	0.76	0.59
10		Mass flow	kg/h	1628	443	169	613	613
11		Mole flow	kmol/h	56	25	10	35	35
12		Volume flow	m3/h	537	166	704	808	1034
13	Mass flows	Mass flow Water	kg/h	0	443	22	464	464
14		Mass flow Azoto	kg/h	1266	1	0	1	1
15		Mass flow Ossigeno	kg/h	362	0	0	0	0
16		Mass flow CH4	kg/h	0	0	6	6	6
17		Mass flow CO	kg/h	0	0	62	62	62
18		Mass flow CO2	kg/h	0	0	70	70	70
19		Mass flow H2	kg/h	0	0	9	9	9
20	Mole flows	Mole flow Water	kmol/h	0	25	1	26	26
21		Mole flow Azoto	kmol/h	45	0	0	0	0
22		Mole flow Ossigeno	kmol/h	11	0	0	0	0
23		Mole flow CH4	kmol/h	0	0	0	0	0
24		Mole flow CO	kmol/h	0	0	2	2	2
25		Mole flow CO2	kmol/h	0	0	2	2	2
26	Mole flow H2	kmol/h	0	0	5	5	5	

Figure 4 - Screenshot of results in the Excel M&EB.xls spreadsheet

## References

1. Daniela Dellepiane, Barbara Bosio, Elisabetta Arato. "Clean energy from sugarcane waste: feasibility study of an innovative application of bagasse and barbojo" 10 February 2003 Journal of Power Sources
2. M. Fermeglia A. Cusicio G. DeSimon G. Longo S.Pricl "Process Simulation for Molten Carbonate Fuel Cells" Fuel Cells 24/08/2004
3. B. Bosio, P. Costamagna, E. Arato, P. Costa, "Modelling approach to fuel cell development", in: S.G. Pandalai (Ed.), Recent Research Developments in Electrochemistry, vol. 5, Transworld Research Network, Kerala, India 2002, pp. 21–45