Chemical Engineering

CUNY The City College of New York

Department of Environment
University of the Aegean

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3-step evolution modeling of the SWPS-GIPO Devolatilization Reactor

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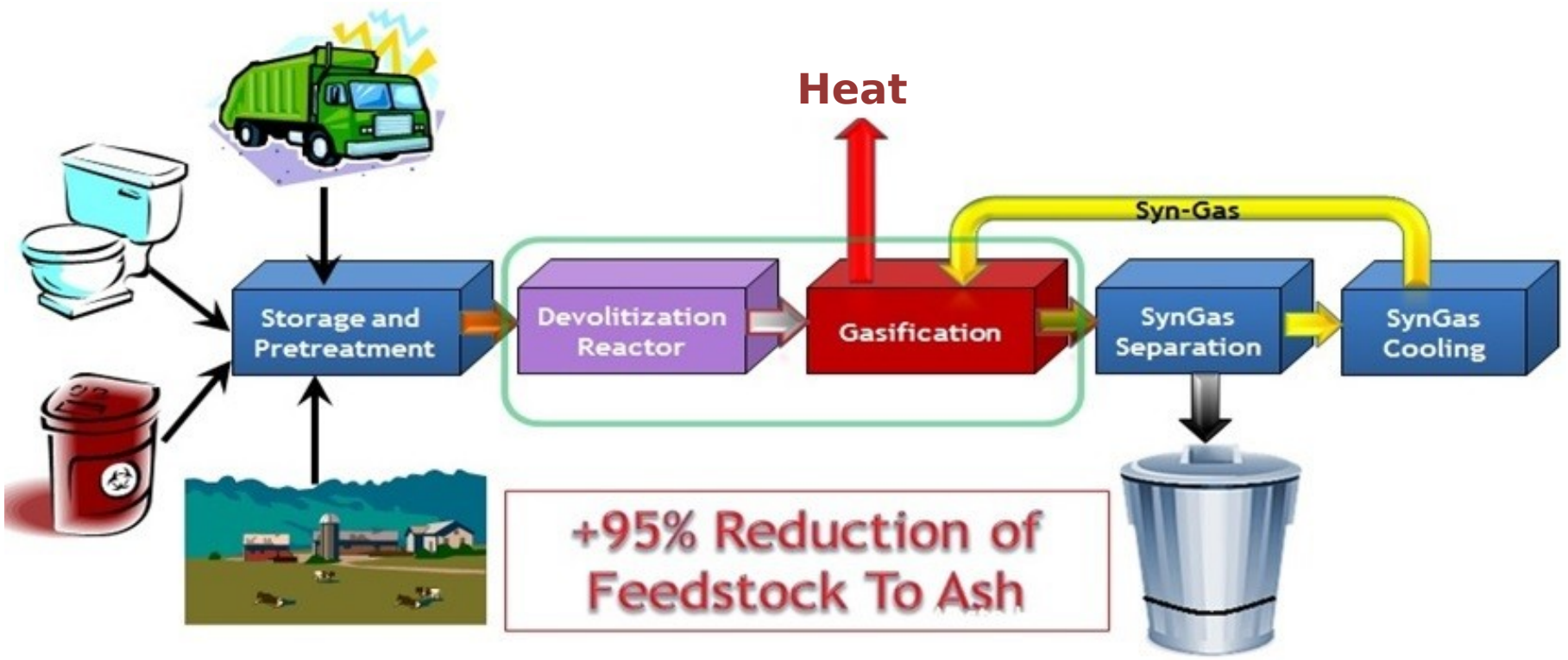
1. Introduction and Scope

The SWPS – GIPO process



Conversion of waste into syngas and heat

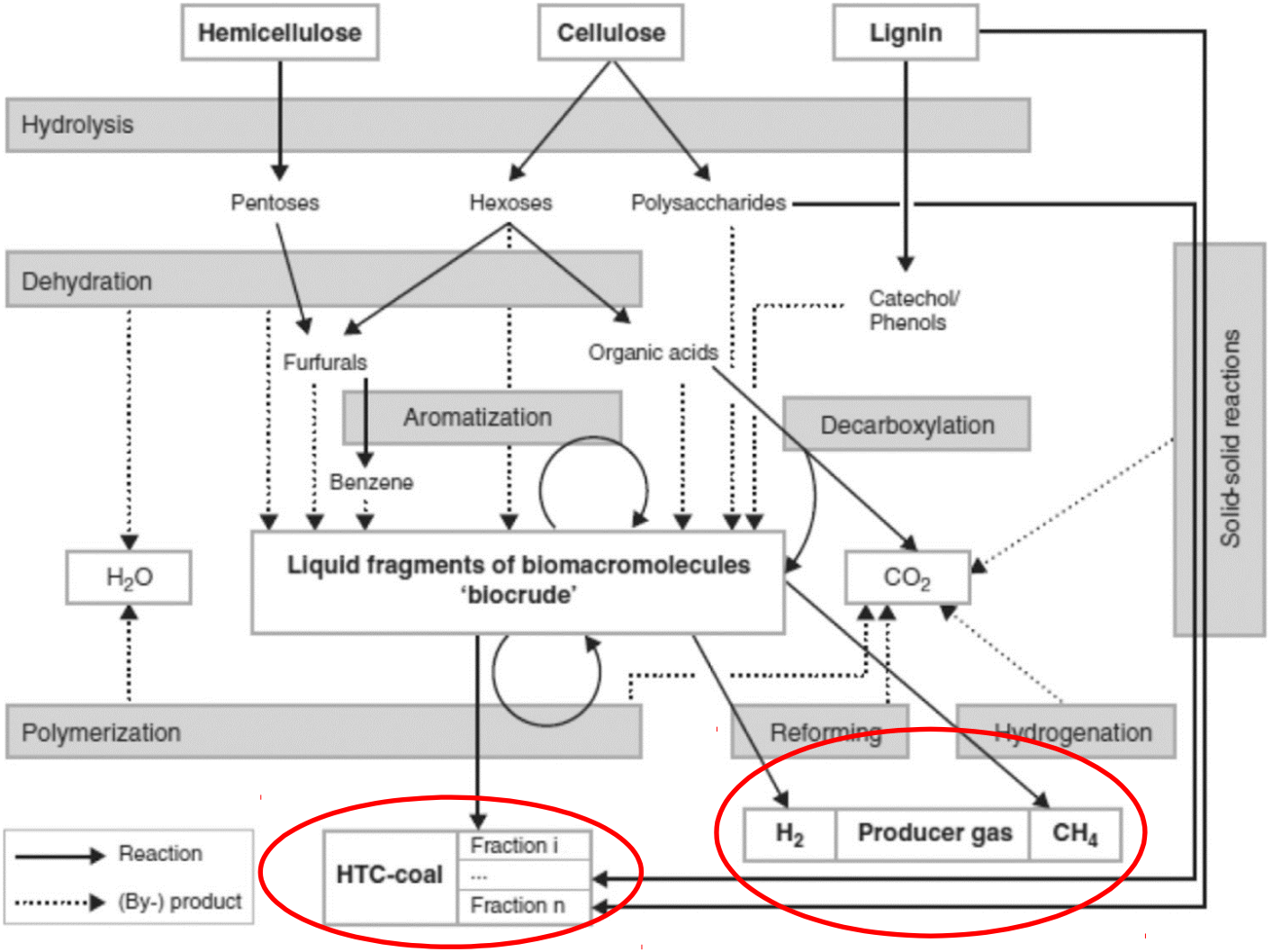
The DVR

- The purpose of the Devolatization Reactor (DVR) is to prepare the wet biomass for gasification.
- The reactor works under high pressures and moderate temperatures and produces mainly a solid carbon-rich product along with gases and liquids.
- “The process maintains saturated water and activates the solid feedstock while removing oxygen via COx”, - MJC
- The operating conditions in the DVR (up to 80 bar & T= 590 K) resemble Hydrothermal Carbonization.

Hydrothermal Carbonization

- Thermochemical conversion technique which is attractive due to its ability to transform wet biomass into energy and chemicals without pre-drying.
- It is also referred to as "aqueous carbonization at elevated temperature and pressure“
  - Usual temperatures of 180 °C to 350 °C and pressures of up to 75 - 80 bar
- The process converts organic compounds into structured carbons

Hydrothermal Carbonization (basic)

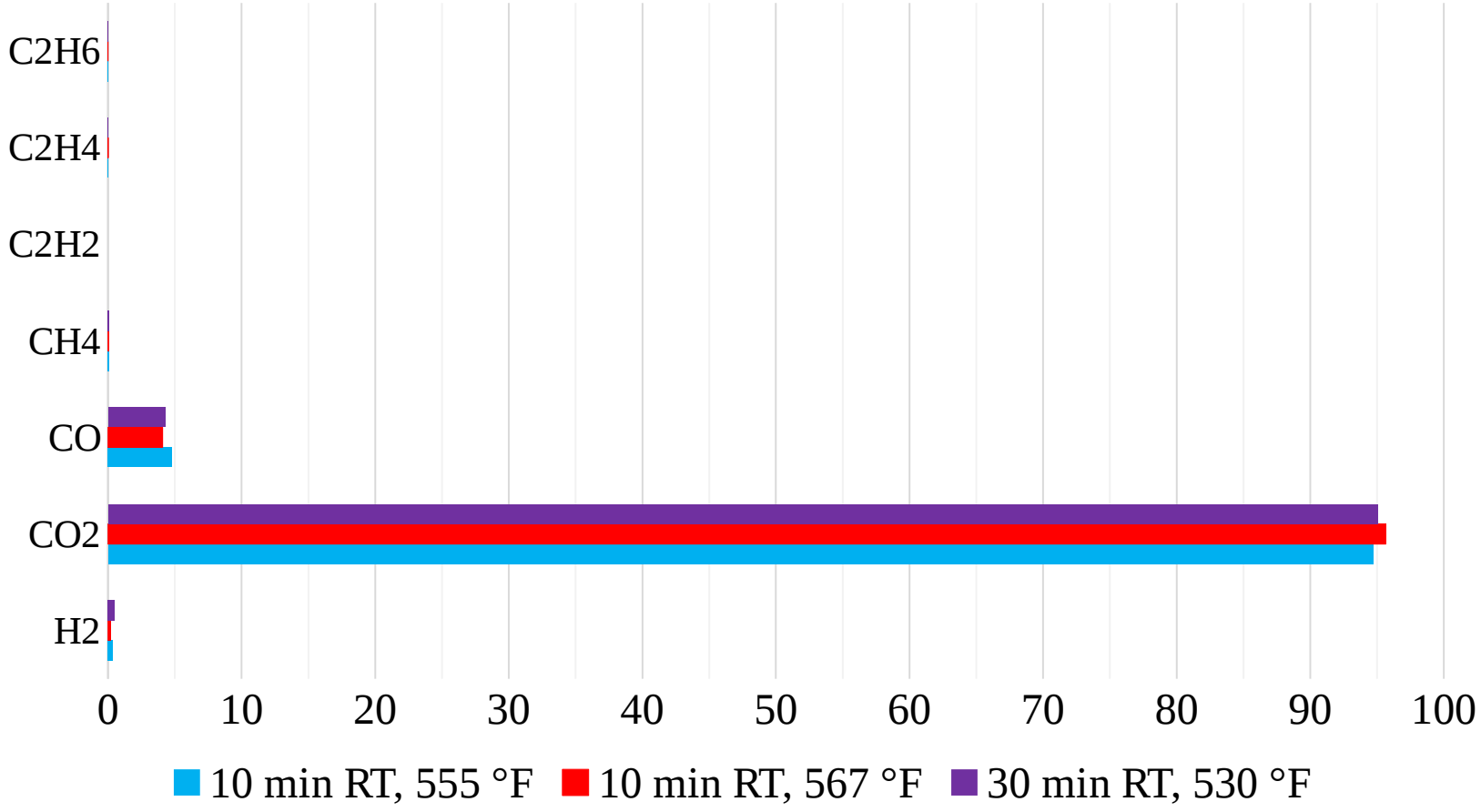


Source: Kruse A, Funke A, Titirici M-M. Hydrothermal conversion of biomass to fuels and energetic materials. Curr Opin Chem Biol 2013;17:515–21.

Status quo and knowledge gap

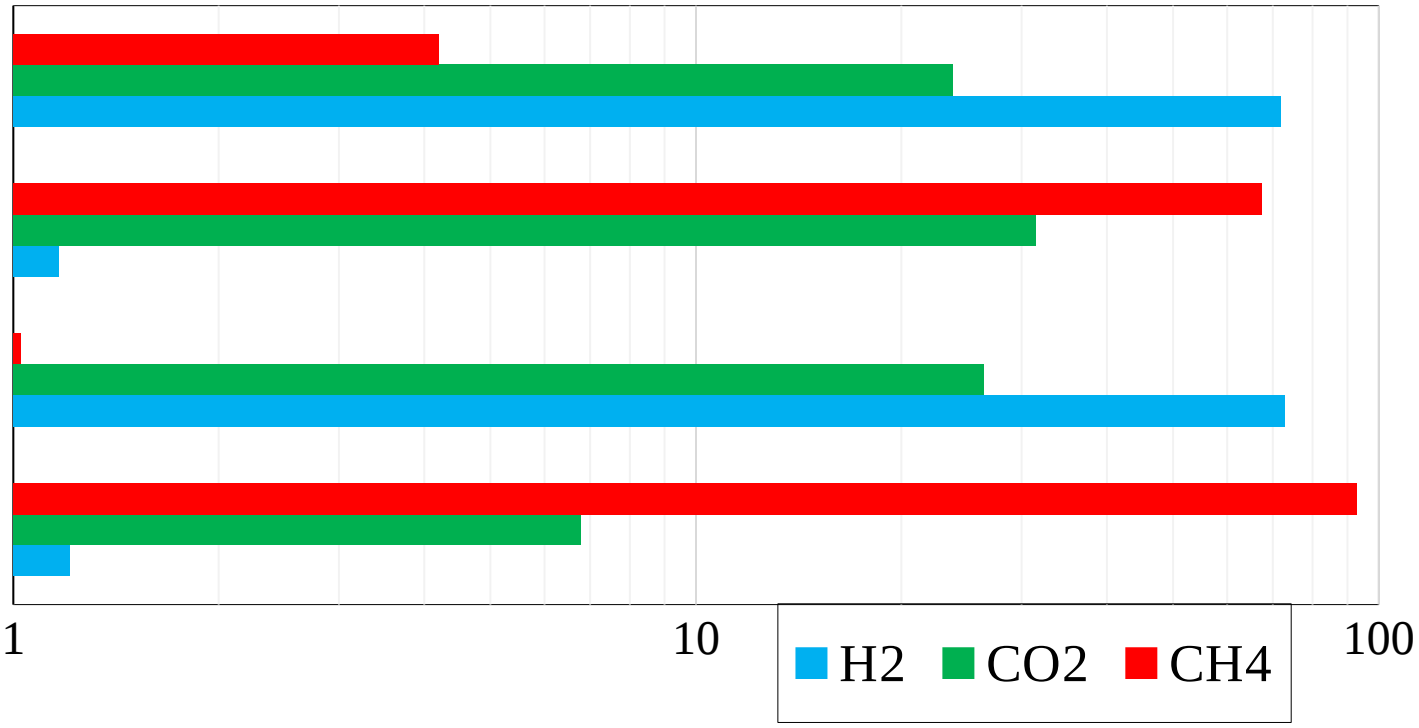
- In HTC/DVR, the processes of hydrolysis, aromatization and and decarboxylation are very well understood.
- The two main questions that are still not fully answered are:
  - How exactly does the solid fraction develop?
  - Why is there such high CO_2 concentration in the final gases? (equilibrium indicates more H_2 and CH_4 production)
- The high CO_2 concentration from the DV process has not been properly modeled or understood.

Results from DVR monitoring*



*Work developed by Ail, S., Sharma, D., Figueroa, J., Sanni, R., Castaldi, *M.J. (2018) Earth Engineering Center, City College of New York*

Examples from DVR models*



- Both equilibrium and modified model show similar trend as Aspen simulation
- In both methods, H_2 or CH_4 is always dominant over CO_2 and CO
- Similar to Aspen simulation, there is over prediction of H_2 or CH_4 composition

*Work developed by Ail, S., Sharma, D., Figueroa, J., Sanni, R., Castaldi, *M.J. (2018) Earth Engineering Center, City College of New York*

Outcome from the analysis *

- Tests were performed at various temperatures (280-315 °C) and residence times (10-30 mins) with 20% and 25% solid chicken manure
- Carbon dioxide is the dominant gas produced (90-95%)
- Carbon monoxide (5-10%), trace amounts of methane and hydrogen
- Aspen and thermodynamic modeling cannot represent accurately the performance of the process; knowledge from literature will help with modifications

*Work developed by Ail, S., Sharma, D., Figueroa, J., Sanni, R., Castaldi, *M.J. (2018) Earth Engineering Center, City College of New York*

Suggested solution

- There are several mechanisms that allow the evolution of oxygen from hydroxide ions due to the favorable system parameters (T, P, PH) – **Examples below**
- Although water is used in excess in HTC, it has been reported that the input and output of water from HTC reaction have been measured to be the similar. Thus, we assume that the reactive oxygen equals the elemental oxygen of the input feedstock.
- We model the generation of hydrochar as a result of gasification char-gas reactions (Boudouard, WGS etc).

Oxygen for hydroxide ions

Example 1

$$S + OH^- \rightarrow SOH + e^- \quad (1)$$

$$SOH + OH^- \rightarrow SO + H_2O + e^- \quad (2)$$

$$2(SO) \rightarrow O_2 + 2S \quad (3)$$

Source: Cox et al., 1990

Example 2

$$OH^- = \frac{1}{4}O_2 + \frac{1}{2}H_2O + e^-$$

Source: Mojovic et al., 2012

2. Materials and Methods

Experimental campaign*

*Work developed by Ail, S., Sharma, D., Figueroa, J., Sanni, R., Castaldi, *M.J. (2018) Earth Engineering Center, City College of New York*

DVR TEST CONDITION: 25% SLURRY, 555 F, 10 MIN. RESIDENCE TIME

Chicken manure slurry, 25% (by mass)
70.92 lb/hr

C	34.11 %
H	4.73 %
N	3.38 %
O	26.01 %
S	0.73 %
Moisture content	10.97 %
Ash	20.07 %
HHV (MJ/kg)	13.8

DVR

Syngas (dry basis)
7.62 lb/hr

Composition	Mol %
H_2	0.39
CO_2	94.70
CO	4.79
CH_4	0.07
C_2H_2	0.00
C_2H_4	0.03
C_2H_6	0.01
TOTAL	100.00
HHV (MJ/kg)	0.38

Water
53.19 lb/hr

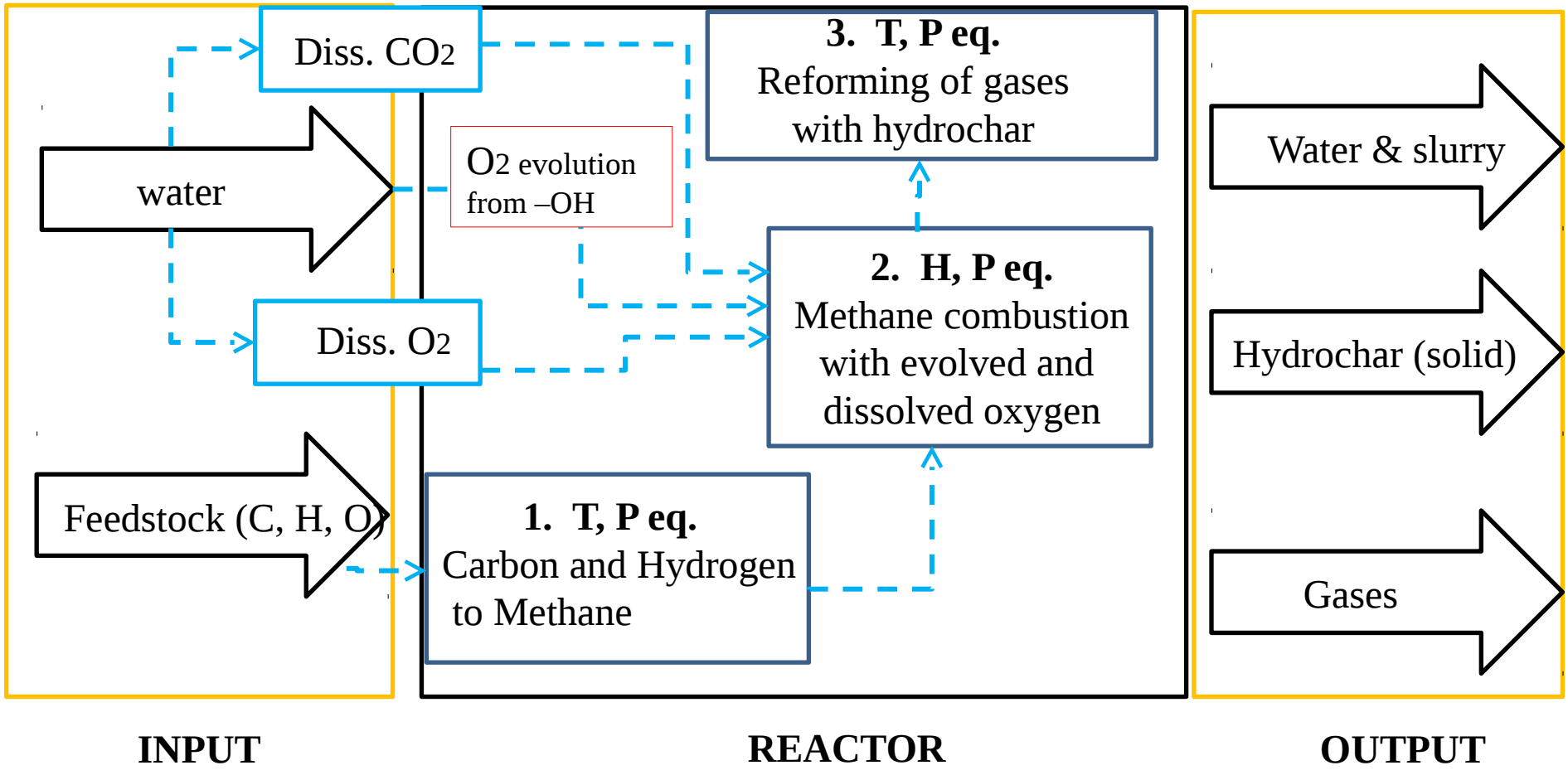
Solid residual
10.09 lb/hr

C	64.79 %
Ash	35.21 %
HHV (MJ/kg)	14.1

Thermodynamic model and solution

- The model is developed in MATLAB/ Cantera
- The method of element potential minimization is used and the model uses a 3-step evolution approach.
- The CO_2 molar fraction is used as an indicator in order to find “how far” is the process from equilibrium and return the results that correspond to the given concentration of CO_2.
- Thus, the solid carbon is calculated in accordance to the result of the final reforming step

Construction of the model



Input feedstock parameters

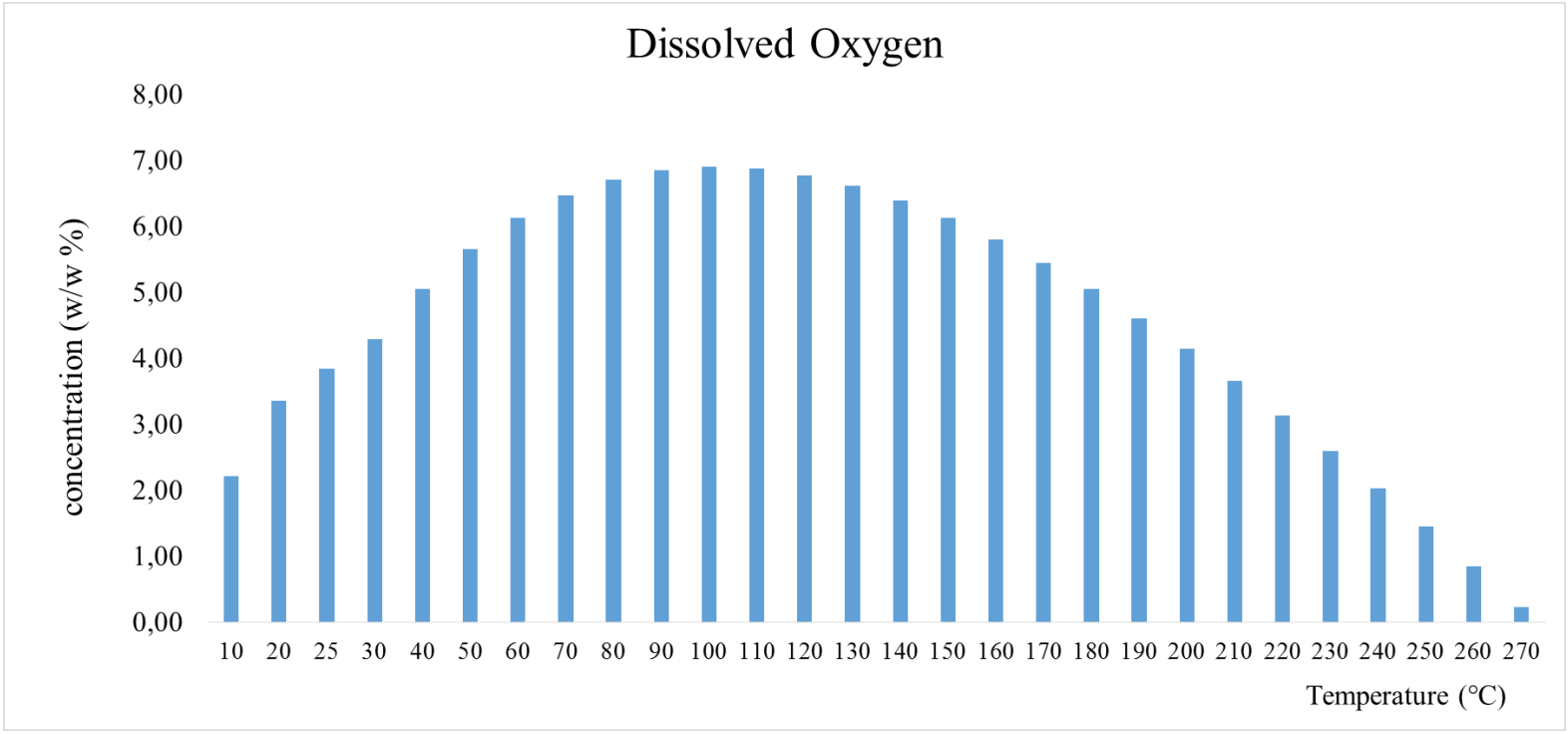
	WBS	Chicken manure	OMWW
Carbon (%)	31.6	35.91	57.3
Hydrogen (%)	4.9	4.98	8
Oxygen (%)	31.9	27.38	23.9
Nitrogen (%)	5.5	3.56	2.3
Ash (%)	26.1	27.4	15.73
HHV (MJ/ Kg)	13.4	15.2	30

Experimentally validated

3. Results

Dissolved oxygen in water

- Dissolved oxygen concentrations are calculated according to the following correlation based on the Henry's Constant for dissolved oxygen at the relevant temperature range
- $H(T) = 761.1 - 108.9 \ln(T) - 40785.5/T$



Source: Qiang Wu, Xijun Hu, Po-lock Yue (2003) Kinetics study on catalytic wet air oxidation of phenol, Chemical Engineering Science 58, 923-928.

Solubility of CO_2 in water

In moderate temperatures (100 – 300 °C) and up to relatively high pressures (100 bar) the solubility of CO2 decreases in respect to ambient conditions.

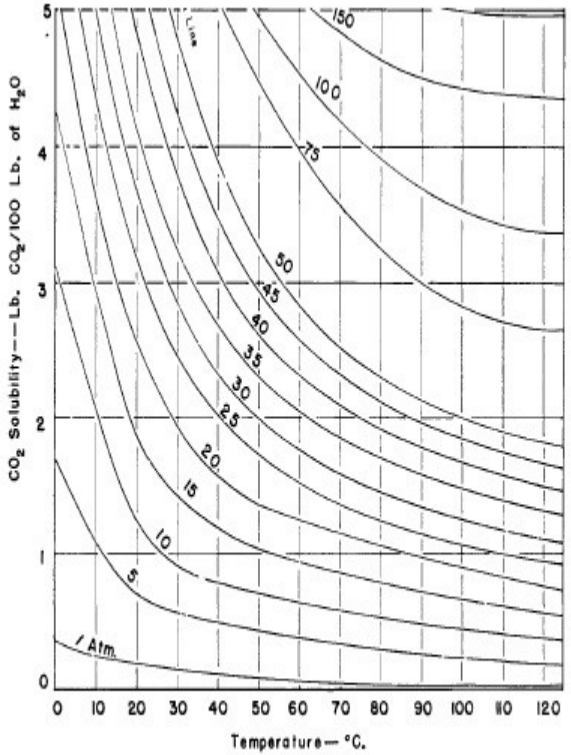
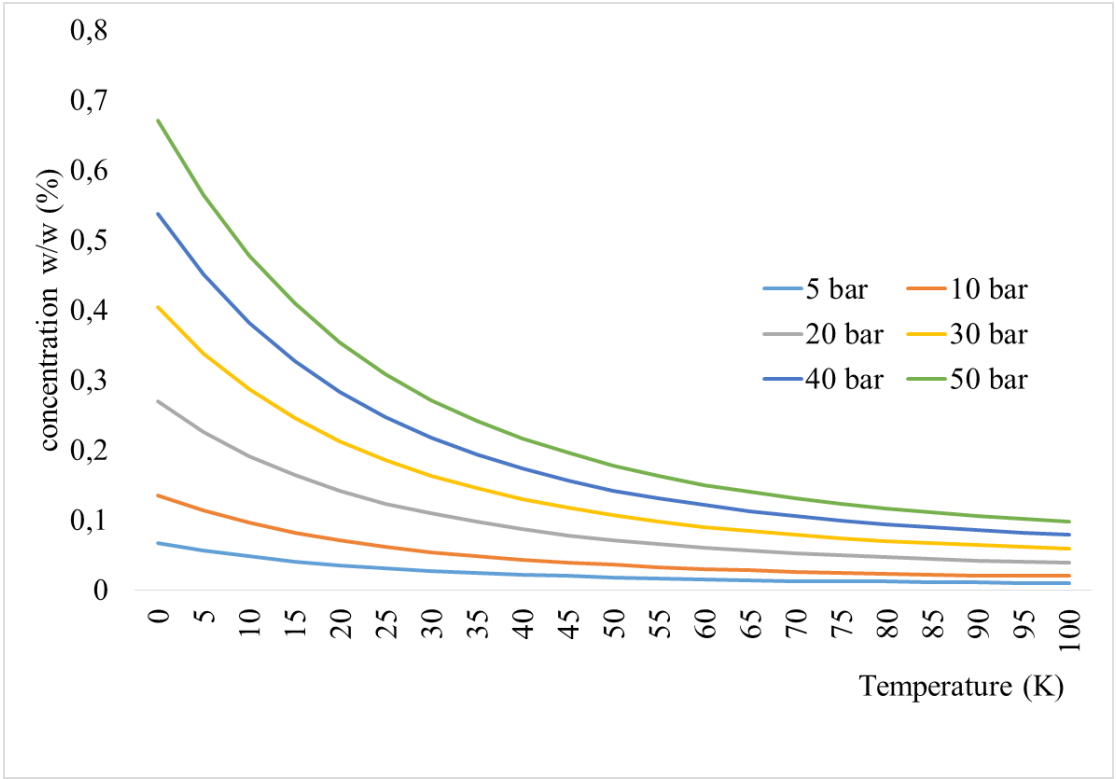
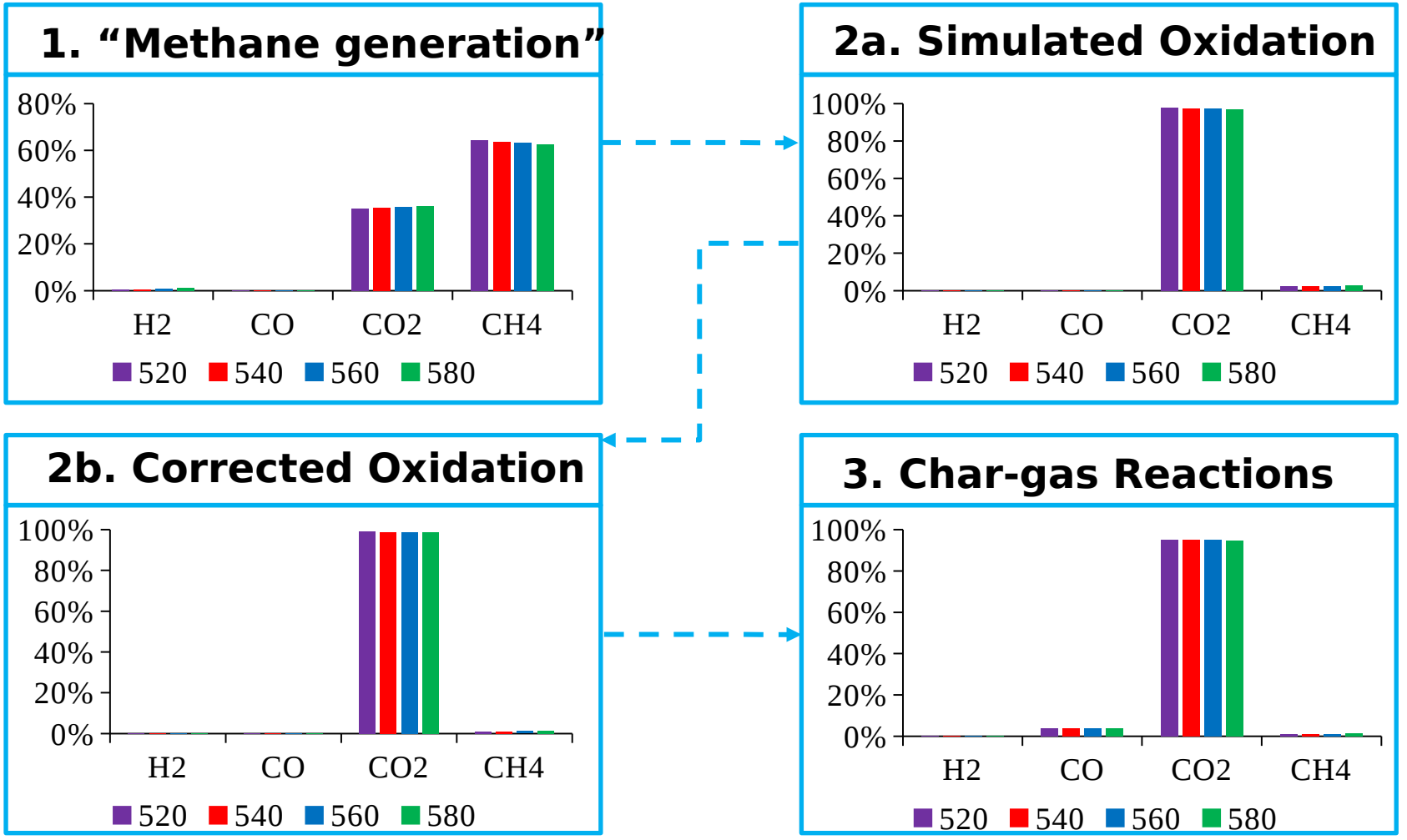


Figure 1. Effect of temperature and pressure upon the solubility of carbon dioxide in water

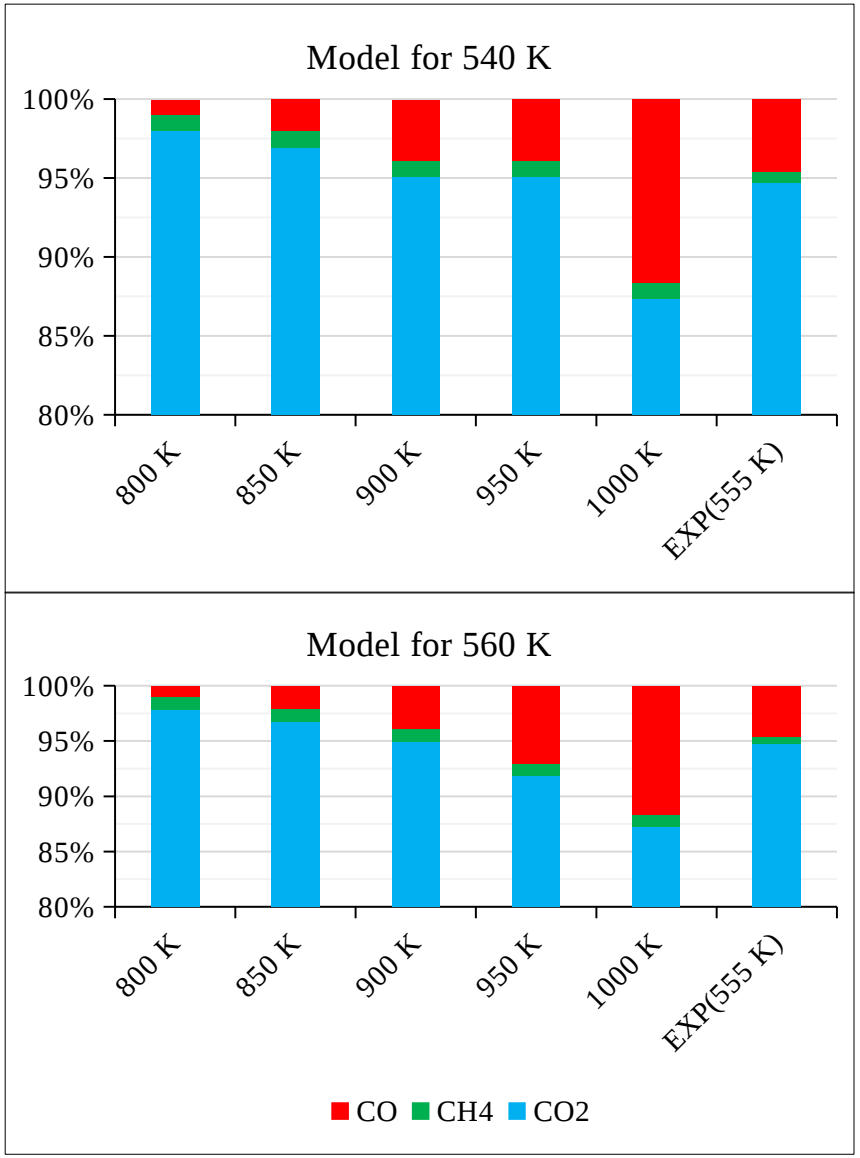


3-step evolution modelling (CM)

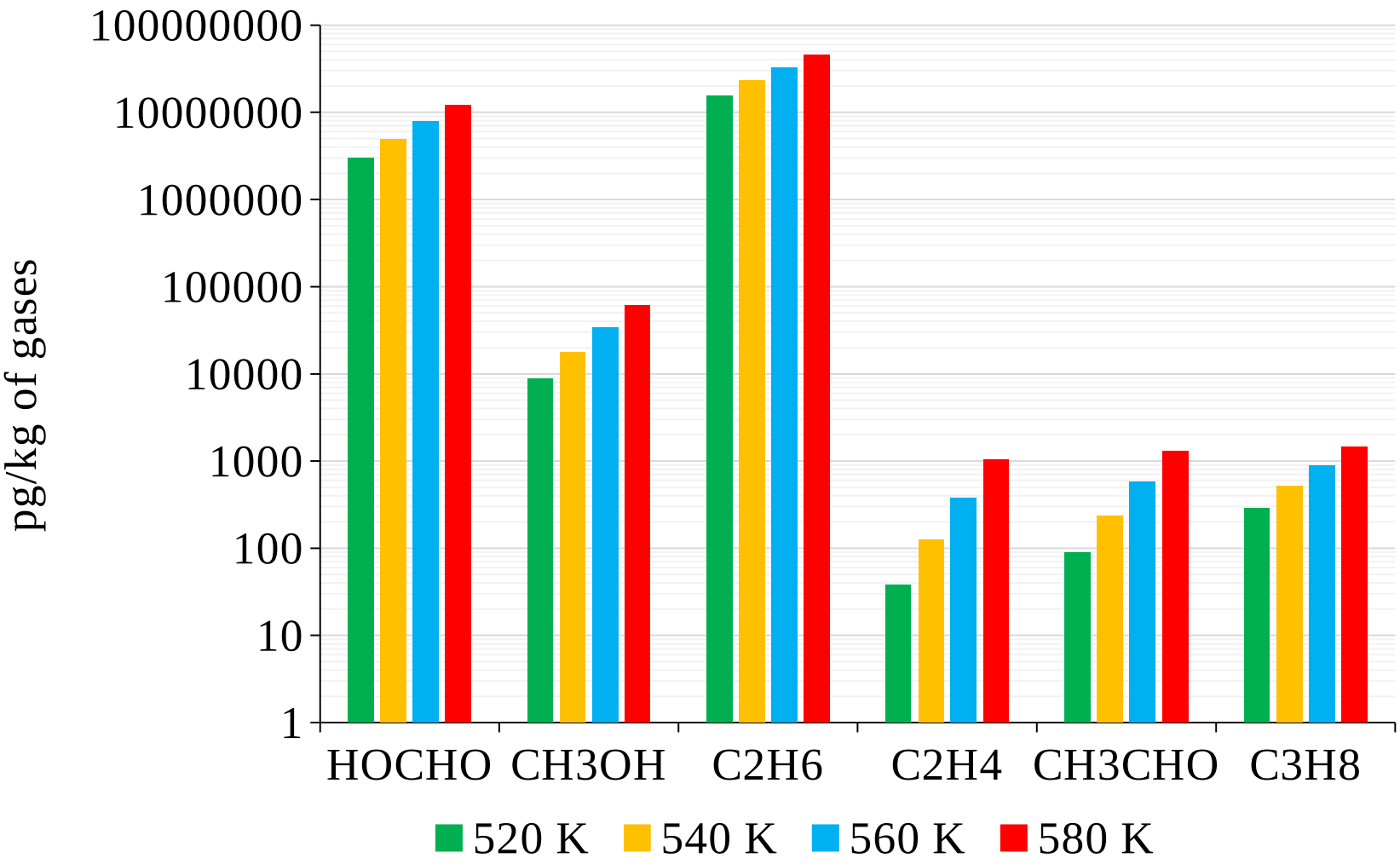


The effect of char-gas reactions (CM)

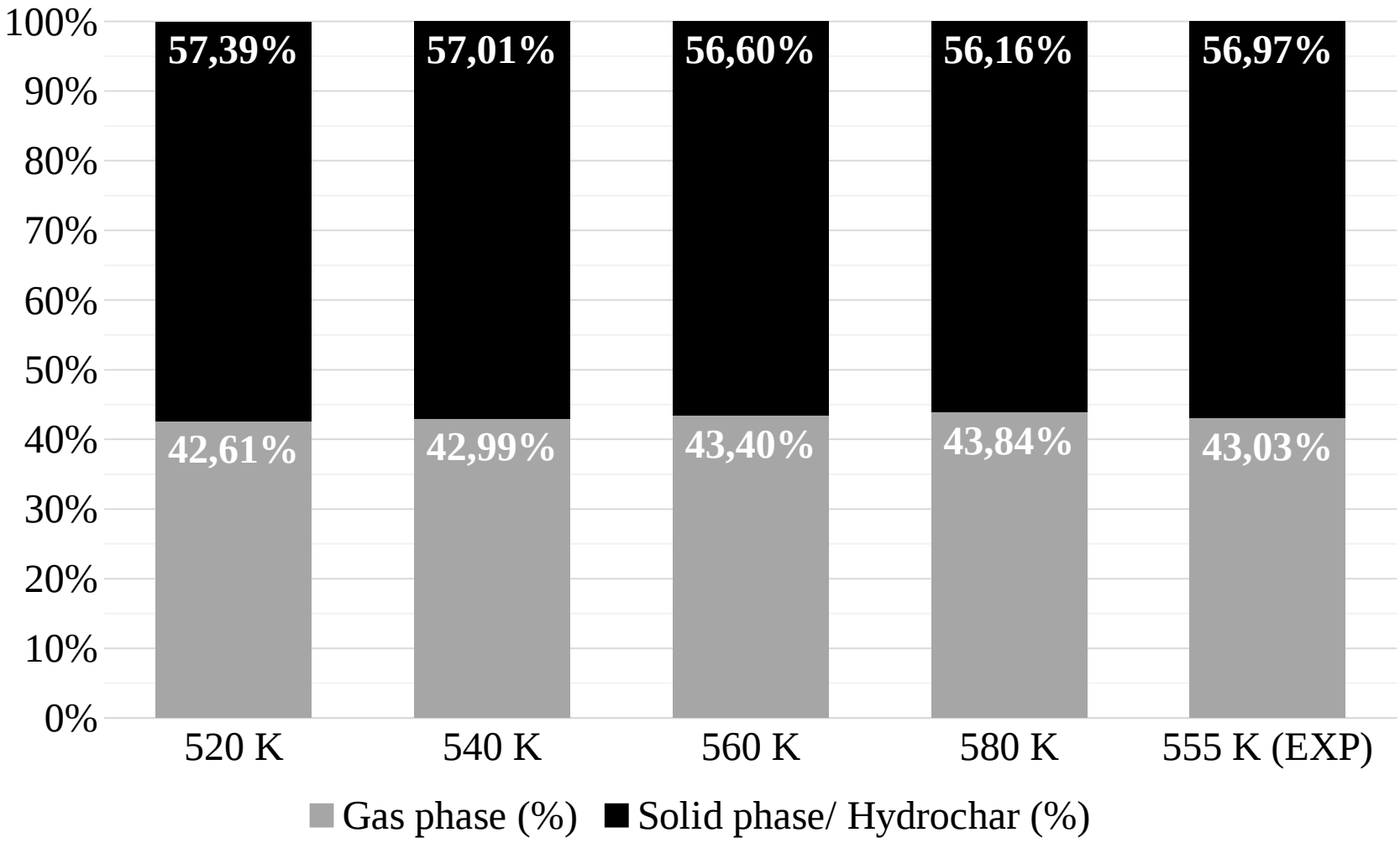
- Modeling results compared with experimental results at 555 K.
- The most representative modeling results are for 540 K & 560 K.
- For this specific case the final correction with char-gas reactions at 900 K produces optimal results
- For modeling at 540 K: CO2:95.05%, CO:3.84 %, CH4:1.05%
- For modeling at 560 K: CO2:94.93%, CO:3.84 %, CH4:1.14%
- Experimental results at 555 K: CO2:94.71%, CO:4.79%, CH4:0.70%



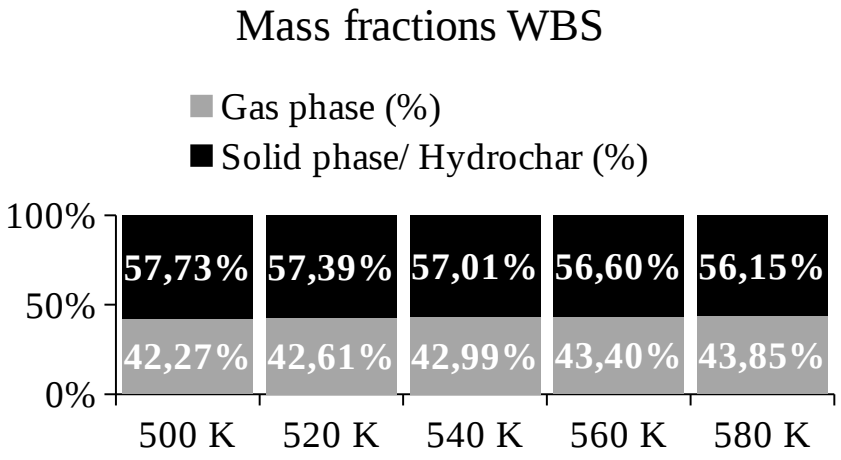
Minor gases

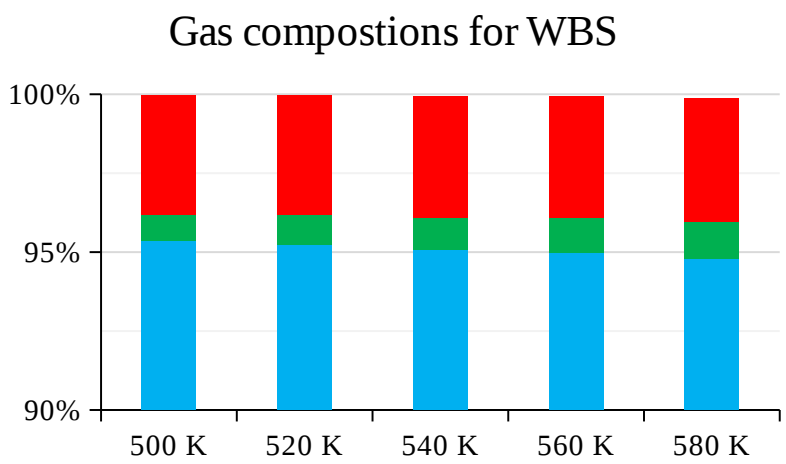

pg/kg of gases
100000000
10000000
1000000
100000
10000
1000
100
10
1
HOCHO
CH3OH
C2H6
C2H4
CH3CHO
C3H8
520 K
540 K
560 K
580 K

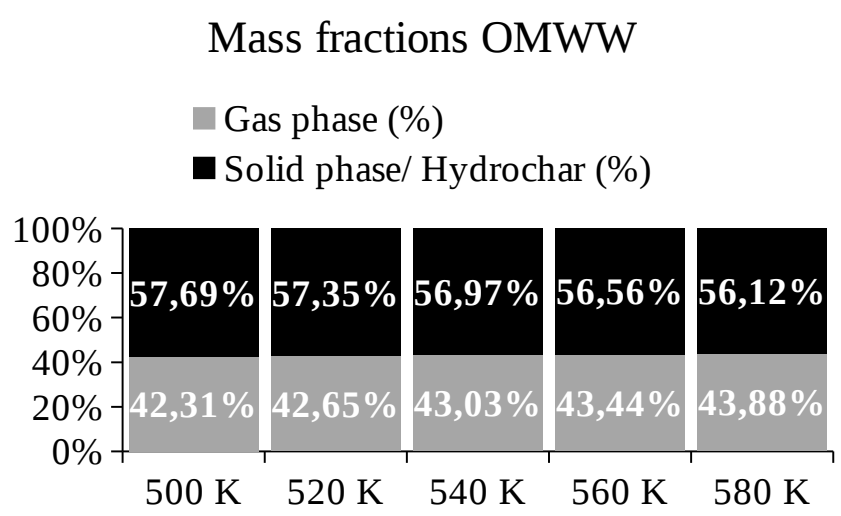
Mass fractions (CM)

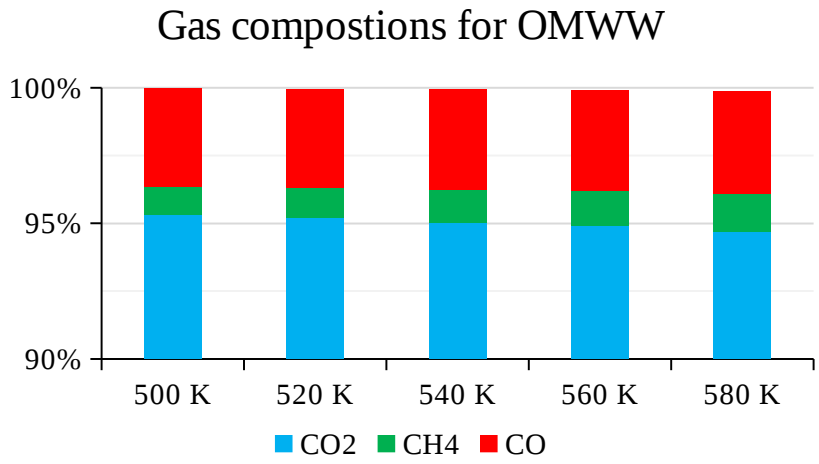


Results for other inputs









Some considerations

- The final reforming (evolution) step can be used as a correction parameter in order to account for the residence time.
- The 3-step evolution model could potentially be used as a method for modelling HTC reactors
  - But this remains as a question for future work
- The use of Cantera software for modelling makes possible the simulation of the whole GIPO process and including the gasification process and the power production.
- Clearly this study recognizes that is only a model, which is a simulation of the actual case and not an exact description of the process.

Conclusions

- By creating a 3 step-evolution thermodynamic model we were able to simulate the operation of the DVR.
- The model results were validated with experimental data obtained at the City College of New York on the GIPO system.
- The final step with char-gas reactions produces optimal results for simulated reforming at 900 K.
- The ultimate scope is to further optimize the quality of the products from the DVR in order to increase the efficiency of the system

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THANK YOU FOR YOUR ATTENTION!

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