Conversion of municipal solid wastes into value-added products as a green alternative in biomass and waste management

INSTITUTO DE CARBOQUIMICA

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

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1. BACKGROUND

- **Billions of MSWs are generated**
- **Generated MSWs is expected to increase**
- **Only ¼ of the total MSWs is recovered**
- **Horizon 2020 expectation: Expensive future task**

(no incineration and landfilling)

PYROLYSIS

Production of liquid, solid and gas fractions that can be used directly either in different energetic infrastructures or as value-added chemicals, providing the necessary energy to support the process.

Results a more environmentally beneficial process than conventional MSWs incineration systems since smaller amounts of NOx and/or SOx can be generated

Offers the opportunity to wash the syngas previously to its application reducing the size and cost of gas cleaning systems.

2. MAIN CHALLENGES

- ✓ To obtain a composition and size as uniform as possible

  - ❑ Pre-processing of the feedstock to make it homogeneous and biologically stable included the following treatments:

a) Saturation in autoclave at 150°C for 15min
b) Extraction of ferric; and non-ferric compounds, impurities
c) Drying process.

Finally, feedstock is transformed in pellet form and was used directly.

- ✓ The addition of low-cost catalysts

  - ❑ Calcined dolomite

- ✓ Lack of information about reactor design and process

  - ❑ Pyrolysis + cracking in a fixed bed reactor

3. Feedstock characterization

Main properties of stabilized MSWs. Left: (proximate analysis, Ultimate analysis and Heating value. Right: Trace elements.

Property	MSWs
Proximate analysis (wt. %)	
Moisture	4.7
Ash	32.5
Volatiles	53.6
Fixed Carbon	7.3
Elemental composition (wt.%)	
Carbon	36.5
Hydrogen	5.2
Nitrogen	1.4
Sulphur	0.2
Oxygen	29.2
HHV (MJ/kg)	14.7

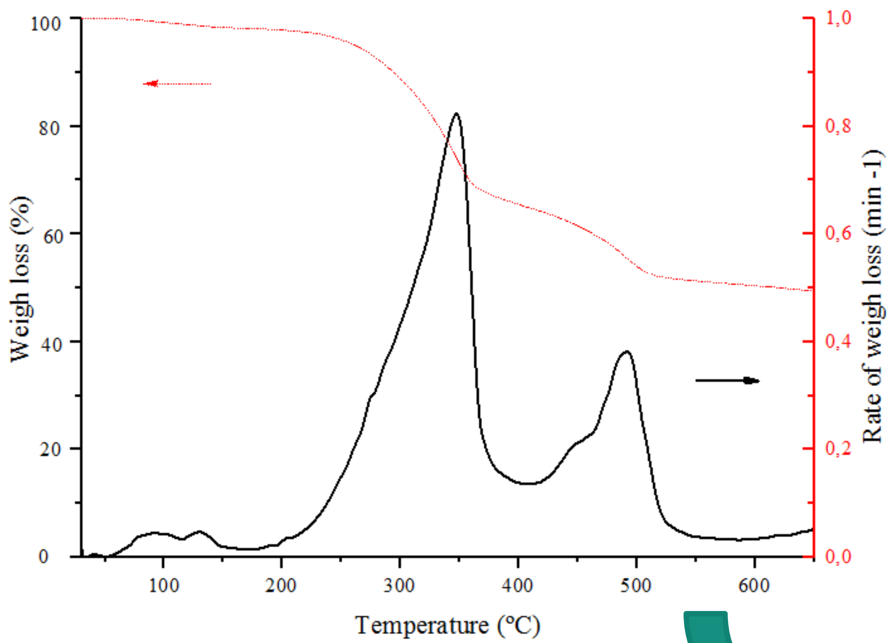
Trace elements	(ppm)
Cl	5600
Al	9984
Ca	52214
Fe	3248
K	9515
Mg	5033
Mn	164
Na	13393
P	3046
Si	65222
Ti	1129

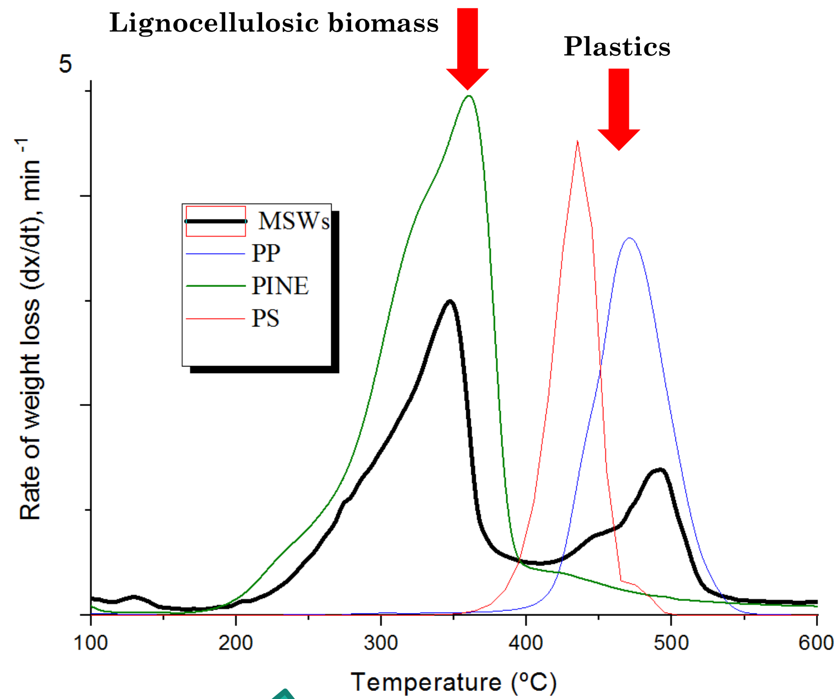
- **Availability (Economic)**
- **Potential value (High Volatile matter and biologically stable)**

✓ **Pyro-Cracking**

3. Feedstock characterization

TGA ANALYSIS





- The sample is composed of different plastic-derived components and biomass

- 550 ºC seems to be sufficient temperature to carry out the devolatilisation of this particular MSWs to complete its total conversion

4. Pyrolysis and cracking reactor

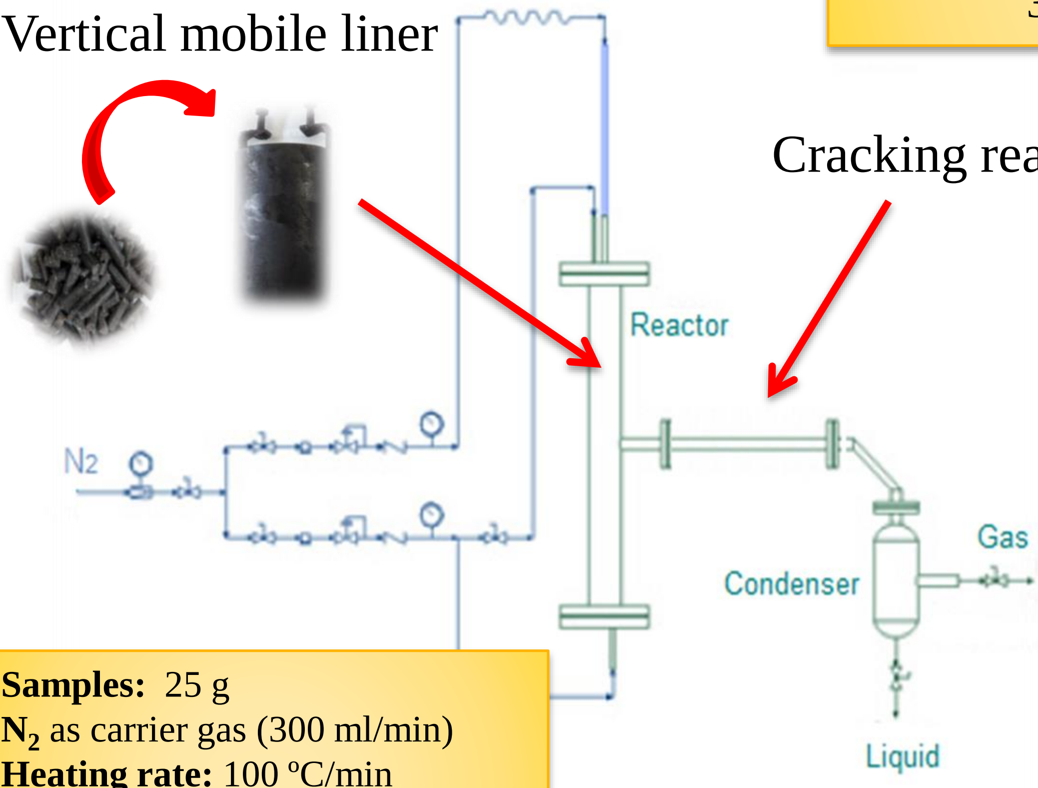
Different temperatures were studied keeping a ratio feedstock to Dolomite on **5:1**

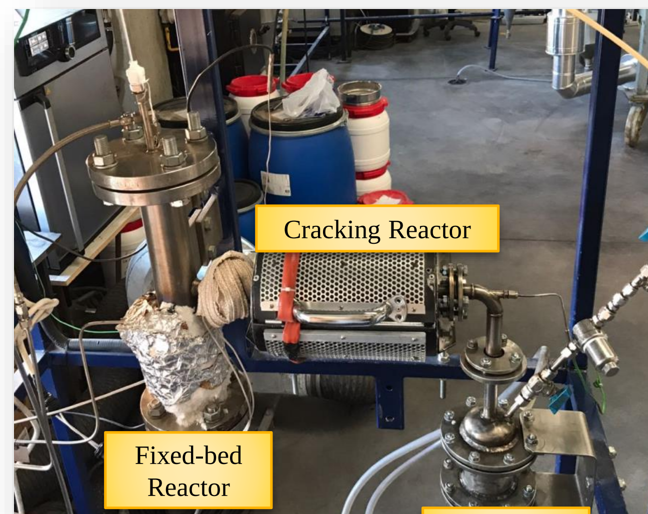
350, 700, 800 and 900 ºC

<u>Fixed-bed + cracking reactor</u>

Vertical mobile liner

Cracking reactor





Samples: 25 g
N_2 as carrier gas (300 ml/min)
Heating rate: 100 ºC/min
Pyrolysis Temp: 550 ºC
Cracking T: 300, 700, 800, 900 ºC
Reaction time: 30 min

5. Products yields

Experimental conditions ($T_{Pyrolysis}$ - $T_{cracking}$ - Catalyst)	Yields (wt %)			
	Liquid	Char	Non-condensable gas	Total
550ºC-350ºC	30.5	50.2	14.9	95.6
550ºC-700ºC	21.9	49.0	25.9	96.8
550ºC-800ºC	14.7	49.1	35.1	98.9
550ºC-700ºC-Dolomite	8.7	49.8	39.1	97.5
550ºC-800ºC-Dolomite	8.5	49.7	41.0	99.3
550ºC-900ºC-Dolomite	6.8	49.0	43.6	99.4
550ºC-900ºC-Dolomite - Cycle 1	7.7	49.5	42.5	99.7
550ºC-900ºC-Dolomite - Cycle 2	8.7	48.1	41.1	98.0
550ºC-900ºC-Dolomite - Cycle 3	7.8	48.1	41.8	97.7

- **Low cracking temperatures led to severe operational problems, where a great part of the liquid was formed by undesired heavy waxes**
- **The higher temperature cracking the lower operational problems were observed and thus, lower liquid yields were obtained**
- **Catalysts action entailed higher non-condensable gases. A greater increase in temperature (900 ºC), was reflected in the highest gas yield (close to 45 wt%) by drastically reducing liquid yields down to 6.8 wt% and therefore, minimizing operational problems**
- **Char yields remained at the same range (50 wt. % approximately).**
- **The yields kept approximately at the same values after several regeneration cycles of the catalyst and no remarkably negative effects were evidenced**

6. PRODUCTS CHARACTERIZATION

CHAR

Property	MSWs
Proximate analysis (wt%)	
Ash	74.7
Volatile matter	12.96
Fixed Carbon	10.43
Ultimate analysis (wt%)	
C	22.6
H	0.6
N	1.0
S	0.6
O	6.5
HHV (MJ/kg)	7.3
LHV (MJ/kg)	7.2

- High Ash content
- Relative poor heating value

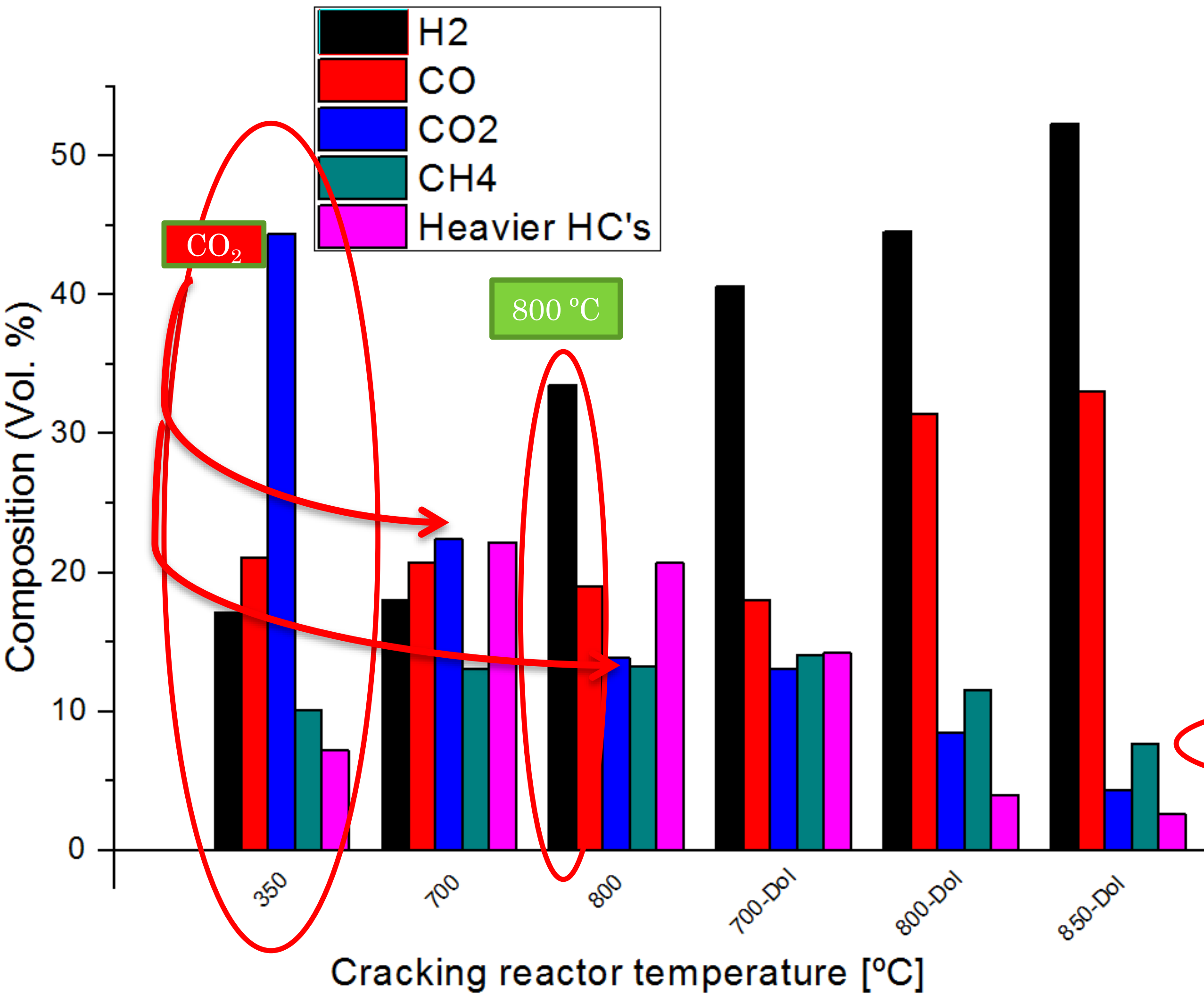
Potential applications

- ✓ As a energy source to cover a part of the thermal requirements of the process.
- ✓ Due to the high ash content: it could be also used cement plants or agricultural soil amendment.
- ✓ As an alternative to reform the pyrolysis volatiles increasing [1]

[1] Wang, N., et al., *Hot char-catalytic reforming of volatiles from MSW pyrolysis*. Applied Energy, 2017. **191**: p. 111-124

6. Products characterization

Gas Fraction



Non Catalytic

- **Low cracking T** : CO and CO_2-rich gas (about 65 vol%) relatively low LHV of 15.2 MJ/Nm^3
- **700-800 °C** :

Reduction in CO_2 down to 19.3 vol% and 13.9 vol%, respectively

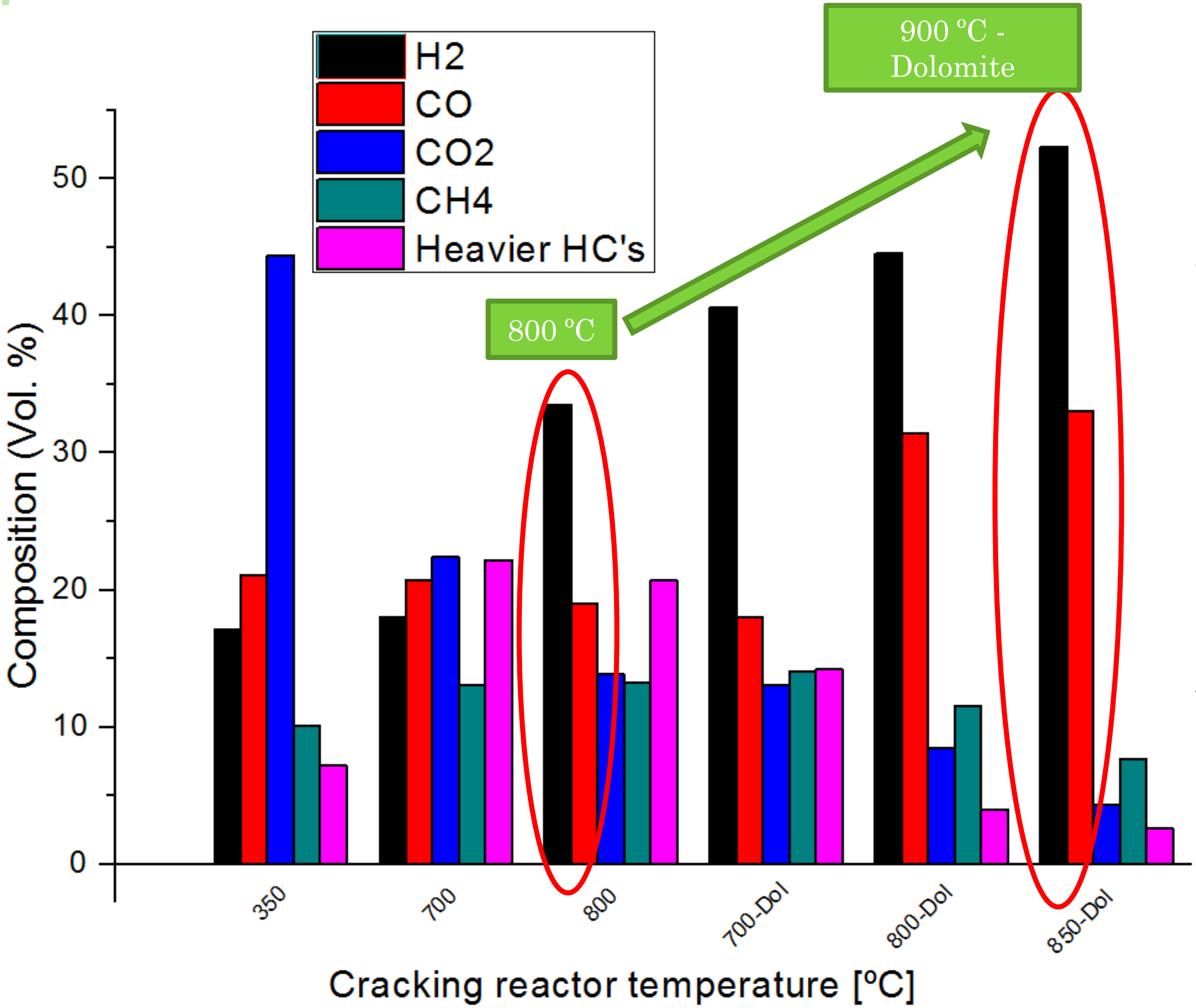
CO composition kept in values close to 18 -20 vol%

H_2 followed an ascendant tendency with T: values close to double (33 vol%)

→ **LHV of 26.5-28.1 MJ/Nm^3**

6. Products characterization

Gas Fraction



Catalytic tests

❑ Greater composition of H_2 and CO as temperature increases

❑ **H_2 production:**

Increases up to 40.6 vol% and 44.5 vol% at 700 ºC and 800 ºC

A half of the gas stream can be considered H_2 (52.3 vol. %) at 900ºC

❑ CO: a crescent tendency

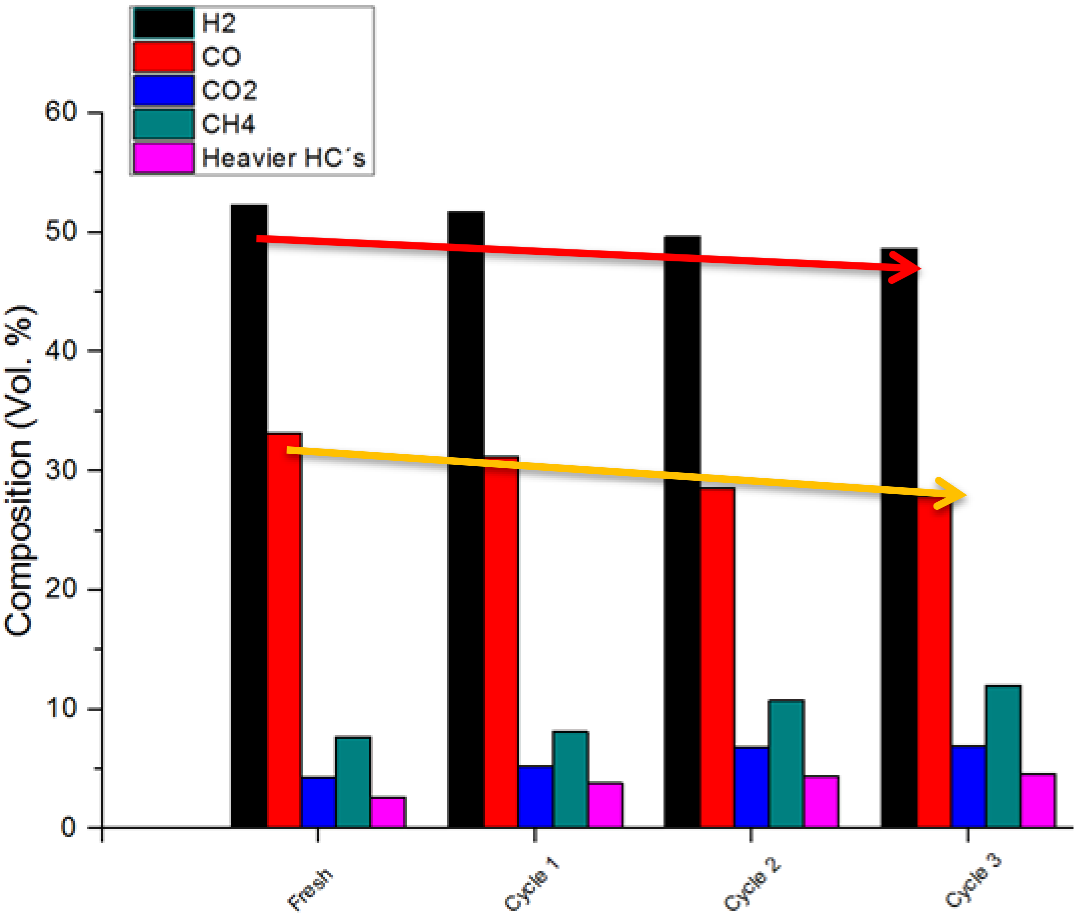
❑ 900ºC:

82 vol% of the total gas stream consisted of CO and H_2

A remarkably environmental issue achievement could be addressed to the reduction of CO_2 and CH_4 with the temperature

7. Study of the life time of the catalyst

Gas fraction

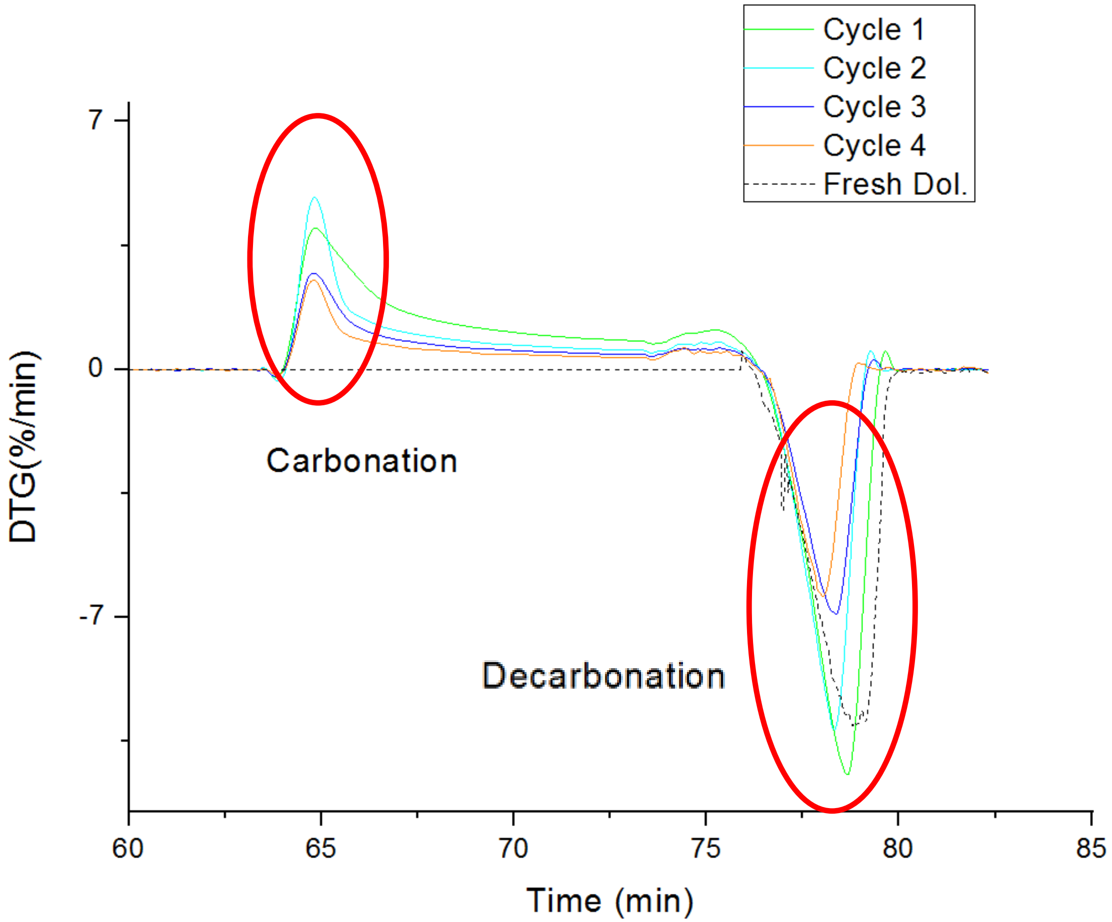


- ❑ H_2 and CO only suffered a slight reduction (close to 5%)
- ❑ CO_2 was maintained at low levels,
- ❑ CH_4 kept in the same range, approximately.
- ❑ **H_2/CO ratio kept in the same range (1.7)**

Not remarkable differences in gas composition and HHV: Only a small negative effect in the process

7. Study of the life time of the catalyst

Catalyst



✓**Carbonation capacity of the catalysts kept at the same range approximately after both first and second cycles.**

✓ After cycles 3 and 4, carbonation capacity of the catalysts was slightly reduced.

✓ The **sintering phenomena** occurred during the regeneration process

✓ It would be necessary to incorporate both a purge and an inlet of catalyst in order to keep on the stability of the catalytic process.

8. NON CONDENSABLE GAS APPLICATION

Gas Fraction

Non catalytic gas

Higher heating value (28.1 MJ/kg)

- ✓ Industrial and domestic boilers
- ✓ Gas engines
- ✓ Gas turbines

catalytic gas

H_2 rich gas
More environmental-friendly

- ✓ Steam boilers (minimization in cost on gas scrubbing devices)

- ✓ Production of methanol, hydrocarbons, ammonia
- ✓ Transportation liquid fuels from Fischer-Tropsch synthesis
- ✓ potential source in the production of H_2

8. CONCLUSIONS

- The pyrolysis + cracking process of MSW seems a good alternative for the production of value-added products, specially a valuable gas fraction that can be used directly as a fuel or as a source of different valuable products.

- The use of an inexpensive and worldwide available catalyst such as calcined dolomite favors the formation of H_2 and CO.

- Particularly, reaching temperatures of 900 ºC in the cracking reactor provides a syngas where more than 80 vol% consists of CO and H_2 with a heating value of 16 MJ/Nm^3.

- The process could be considered relative inexpensive due to the potential of the obtained char to contribute to the necessary energy requirement of the process.

THANK YOU FOR YOUR ATTENTION!!

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