Catalytic Effect of Char for Tar Cracking in Pyrolysis of Citrus Wastes, Design of a Novel Experimental Set Up and First Results

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This study describes the design of a novel fixed bed lab scale down-draft 'multiple layer' reactor, aimed to investigate the effect of chars as means to catalyze tar cracking during pyrolysis of agro-industrial wastes.
Preliminary experiments were carried out on pyrolysis of citrus wastes at 500, 700 and 800 °C for 30 minutes holding time in N_2 atmosphere. Tar obtained from pyrolysis of same feedstock at 650 °C and 800 °C were used as cracking catalyst.
Tests showed that tar yields of pyrolysis of approximately 2 g of oven dried lemon pulp could be reduced when approximately 0.4 g of chars were used as a catalytic means. Results of runs conducted at 500, 700 and 800 °C show no significant cracking effect at the lower temperature and a moderate (3% reduction in tar yield) at the higher temperatures.
Results show that catalytic effect of char may be foreseen in downdraft set-ups but mainly in sections close to the gasifying zone.
Overall, the system described showed to be a valid tool in evaluating the effectiveness of using chars in tar cracking during pyrolysis of citrus wastes. Moreover, important insights were obtained for future more in depth analyses of the issue.

1. Introduction

Pyrolysis is a thermo-chemical process commonly used to reduce solid biofuels, such as residual biomass, in a mix of solid (chars), vapors (tar) and gases. In reactions aimed to obtain gases destined to engines for the production of electrical energy, such as in downdraft gasification, pyrolysis occurs right above the gasification sections and tars are undesired products, which need to be cracked.
Whilst systems to efficiently crack tars in gasification set-ups are required (Monteiro Nunes et al., 2008), tar cracking is often complex and this hampers the widespread diffusion of small scale gasification systems. However, downdraft gasification is considered one of the potentially most economically viable process to produce decentralized electricity generation in small scale applications (Ahrenfeldt et al., 2013 and Biagini et al., 2014).

2. Materials and methods

2.1 System set-up

The reactor consists of a vertical tube heated by an eternal furnace. A lay-out of the complete system is reported in Figure 1. It consists of: (1) a cylindrical stain steel (AISI 316) reactor, 365 mm long, 38 mm external diameter and 30 mm internal diameter, (2) fittings and thermocouples, (3) flow meter, (4) tubular furnace, (5) temperature regulator and controller, (6) electrical power transformer, (7) cold traps, (8) ball valves, (9) bubbler and (10) hood.
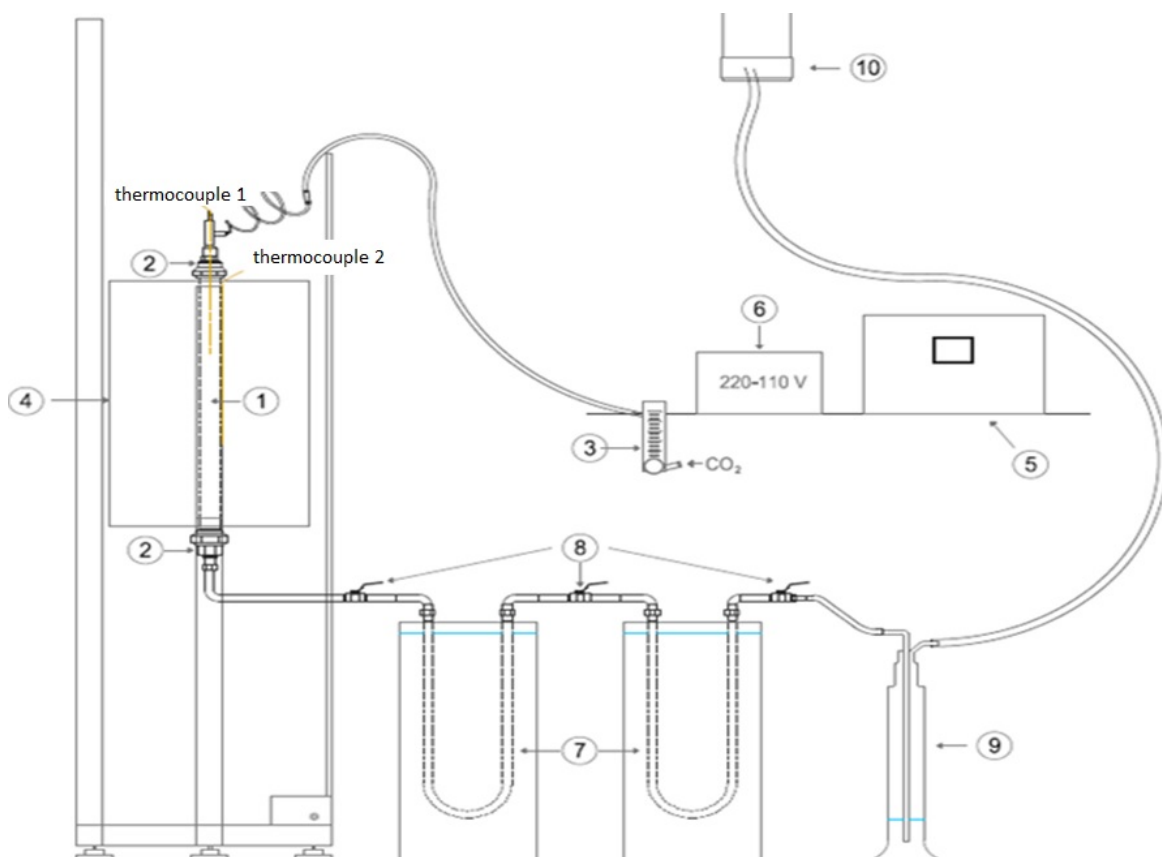
Figure 1: Reactor general set-up

The novel feature incorporated in the reactor relates to the sample holding arrangement. Different samples may be placed in a number of maximum three crucibles placed one above the other inside the main tube (see Figure 2). A vertical downdraft flow of N_2 is used as carrier medium to sweep away pyrolysis products.

Each crucible is open at the top end and has an open wire mesh at the bottom end (see Figure 3), this way carrier gas can flow through the samples and products (vapors and gases) are released via the bottom wire mesh.

Approximately 2 g biomass are placed in the crucible upstream and two samples of approximately 0.2 g each of char are placed in the center and bottom crucibles. In this configuration the vapor and gases which are released by the biomass placed in the top crucible, flow through to the second crucible where they hit the first hot char sample and react with it.

The reaction products are then released through the wire mesh at the bottom of second crucible and carried down to bottom crucible where another approximately 0.2 g of char is placed.

Final products are then swept away through a set of two cold traps placed in a bath of a mixture of ethylene glycol, water and dry ice kept at approximately - 25 °C, used to condensate all tars before gases are vented into the hood.

The assembled reactor, Figure 2, is placed in a furnace whose temperature is raised to the desired value at a rate of 50 °C/min and kept for a holding time of 30 minutes.

A thermocouple placed just above the biomass sample in the first crucible controls that feedstock reaches the desired temperature and monitors it during the reaction.

The analyses are aimed at evaluating the tar cracking effect of the bed of char placed in the centre crucible. This is calculated via the differences in tar yields between the configurations with and without chars in the bottom two crucible, but also via differences in physico-chemical properties of the two chars samples placed at centre and bottom crucibles.
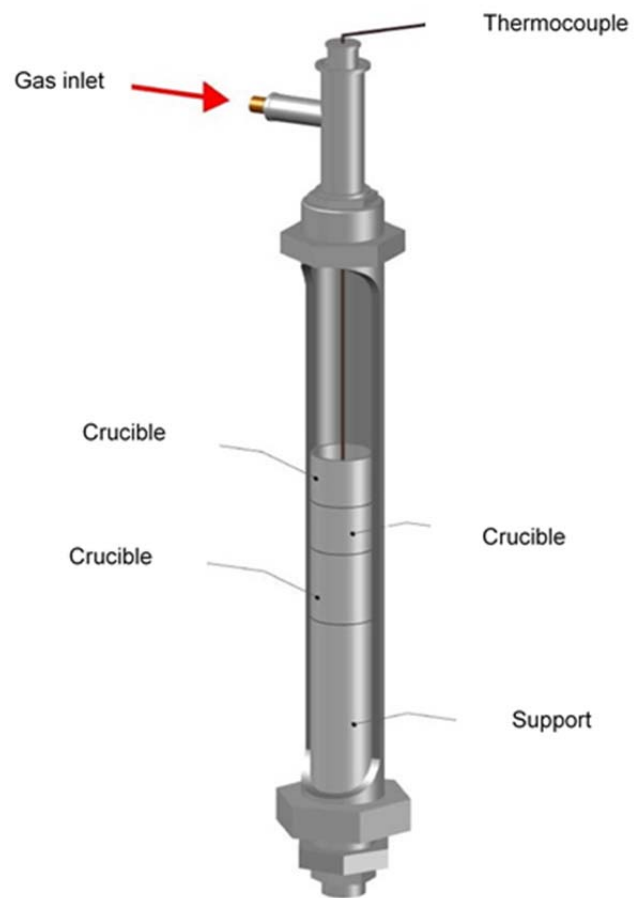
Figure 2: assembled reactor

Figure 3: Reactors crucibles

2.2 Raw material and sample preparation
Each run two type of feedstock is prepared: 1) raw biomass to be placed in the top crucible and 2) char placed in centre and bottom crucible. The raw biomass is prepared as follows: raw lemon pulp collected at an orange juice factory in province of Messina, Sicily. The raw citrus pulp showing a moisture content of approximately 80 % is oven dried then milled and sieved to select the portion between 200 and 850 µm.
Once dried, the citrus pulp showed an equilibrium moisture content between 2.7 and 3.0 %. The feedstock is then kept oven dry prior to each experiment.
Char to be placed in center and bottom crucibles are prepared following the procedure reported in (Volpe M. et al., 2015) in a horizontal fixed bed quarts batch set up described in (Volpe M. et al., 2014). Two temperatures chars are prepared: 650 °C char for runs at 500 °C and 800 °C char for runs at 700°C and 800 °C.
The aim is to minimize any reaction of char itself, hence check only its reactivity in contact with hot tars generated from biomass sample.

2.3 Experimental runs
Experiments are performed to set-up the system, to test the reproducibility of results and the general validity of the method. Two sets of pyrolysis runs are conducted, with nitrogen as a carrier gas at 1.0 l/min flow rate at 50 °C/min heating rate respectively at 500, 700 and 800 °C peak temperatures and 30 min holding time. At end of run the reactor was left to cool naturally to room temperature and products collected to calculate solid and liquid yields. Gas yields were calculated by difference to close the mass balance. Tars were collected as reported on a previous work (Volpe M. et al., 2014).
Each set of runs performed in duplicates is conducted in the following sequence: 1) char in the center crucible only, 2) chars in two bottom crucibles, 3) biomass only in the top crucible 4) biomass in top crucible and chars in the bottom two. The char only runs are performed to calculate the intrinsic reactivity of chars in the present set-up so to allow evaluation of the net cracking effect in biomass and chars runs.
Given the small amounts of chars used, particular care was taken in taking into account the moisture intake of chars during experiments preparation and sample collection after runs. Moisture intake of feedstock could be significant even in the relatively small time needed for handling (Messineo et al., 2012, Messineo et al., 2014). Chars, in particular, may intake significant amounts of structural moisture reportedly due to the presence of ultramicropores (Titirici, 2012). Moreover, due to fresh chars originated by polymerization of tars on existing hot particles in center and bottom crucibles, chars are bound to intake different amounts of moisture prior and after the experiments. Potential errors related to non-consistent account for moisture intake have been minimized by reducing the handling times as much as possible and by preventive calculation of moisture intakes in different chars in the laboratory environment. Values lower than 1% (w/wdb) were consistently observed.

3. Results and discussion

Results are reported for runs 1) biomass only, 2) biomass and char in center position and 3) biomass and chars in centre and bottom position.
Table 1 reports results for runs at 500 °C. Runs with chars only (not shown here) show same yields reported in present results. This demonstrates that net effect on chars in center and bottom positions are negligible at 500 °C peak reaction temperature.

Table 1: Pyrolysis residues mass yields (MY) of Lemon Pulp at 500 °C; *run* 1-3

	Residue	Run 1- MY [%]	Run 2- MY [%]	Run 3- MY [%]
Biomass	Char	35.00	35.60	35.57
	Tar	10.86	10.52	9.94
	Gas*	54.04	53.87	54.47
Char pos. 1	Char		97.74	97.02
	ML		2.25	2.97
Char pos. 2	Char			97.73
	ML			2.26

* by difference

Results reported on Table 1 show the total yields (average out of duplicate or triplicate runs) per each of the crucible position and the mass loss percentages (%w/w db) (ML) of the chars in the holders 2 and 3. Blank

cells indicate no feedstock in crucible. Results show no apparent tar cracking effect at 500 °C: tar yields do not seem to change significantly when char is placed in center and bottom crucibles. Noticeably chars placed in center and bottom crucibles, recovered after runs, showed a 'sticky' appearance probably related to the polymerization of tars on hot particles (samples in chars only experiments did not show the same behavior)

Table 2: Pyrolysis residues mass yields (MY) of Lemon Pulp at 700 °C; *run* 1-3

	Residue	Run 1- MY [%]	Run 2- MY [%]	Run 3- MY [%]
Biomass	Char	33.07	32.75	33.14
	Tar	11.21	9.75	8.11
	Gas*	55.70	57.49	58.74
Char pos. 1	Char		97.58	99.08
	ML		2.41	0.91
Char pos. 2	Char			98.69
	ML			1.30

* by difference

Results at 700 °C begin to show a moderate cracking effect. Table 2 shows that a 3% reduction in tar yield is observed when char is placed in center crucible. Note that char yields in center and bottom positions (not shown here) are similar or slightly higher than those obtained in char only runs (chars in center and bottom crucibles and no biomass in top crucible). In fact, chars do release some volatiles during runs (mass yields are consistently around 95-96%), however, when biomass is in place, the data show that 'net effect' is null or slightly positive (2-3% w/w% db). Thus, the compounds polymerized on hot char (as consequence of cracking) (Volpe R et al., 2015) and the amount of volatiles released by char, balance out or slightly favor polymerization.

Table 3: Pyrolysis residues mass yields (MY) of Lemon Pulp at 800 °C; *run* 1-3

	Residue	Run 1- MY [%]	Run 2- MY [%]	Run 3- MY [%]
Biomass	Char	31.98	32.31	32.45
	Tar	8.73	9.49	8.95
	Gas*	59.27	58.19	58.58
Char pos. 1	Char		98.60	98.47
	ML		1.39	1.52
Char pos. 2	Char			99.50
	ML			0.49

* by difference

When reaction temperature is raised to 800 °C, the above described phenomenon is yet more prominent. The apparent mass loss of char placed in center crucible is reduced to 1-2%, thus indicating that some higher deposition (polymerization) or heavier compounds occurred on hot chars.

All data demonstrate that in this set up, chars are reactive with tars above 500 °C and that hot volatiles released by biomass are polymerized on hot chars increasingly as the reaction temperature is increased.

It is worth noting how results are significantly 'reactor-specific'. The same feedstock returned significantly different results when treated in a different set-up (Volpe M et al. 2015). it is well known how, behavior of biomass may change significantly depending on different set up and reaction conditions (Morgan and Kandiyoti, 2014). Pyrolysis of Lemon pulp in a horizontal quartz retort showed similar char yields (35-35% w db) but significantly different liquid and gas yields, respectively 38-39 % versus the present 8-10% liquid yield and 25-28% versus the present 54-55% gas yield. It is evident that some char gasification due to production of native reactive gases is occurring in this set up (Dabai et al, 2014).

4. Conclusions

The proposed set-up is proved useful to detect a tar cracking effect by char in simulated downdraft systems. The data show that the effect is appreciable for temperature above 500 °C and are reportedly more evident for temperatures above 700 °C.

This shows that in a larger scale downdraft gasifiers, where gasification occurs at 900-1000 °C, chars may react with tars produced in the above sections of the gasifier, but only in the zones close to the gasifying sections.

Whilst recent studies report the char catalytic effect in tar cracking (Dabai et al., 2014), this work contributes to shed some additional light into the complex dynamics that govern the operation of downdraft gasifiers. Some additional experiments are currently being conducted on the char used as cracking media in order to further qualify the onset of reactions occurred between solids and hot vapors in the present set up.

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