CATALYTIC CO-PYROLYSIS OF GRAPE SEEDS AND WASTE TYRES AS A LOW-COST STRATEGY IN THE PRODUCTION OF HIGHT-QUALITY BIO-OILS

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ABSTRACT

The concept of biorefinery emerges as a promising alternative to reduce environmental impact caused by extraction and processing of fossil fuels. In that sense, the use of renewable sources and, more specifically, the use of lignocellulosic biomass is one of the best promising alternatives since it is the only carbon-containing renewable source that can produce biofuels similar to fossil fuels and it does not compete with food production. Among all the processes that can valorize lignocellulosic biomass, pyrolysis is an attractive alternative because it is the only thermochemical process that can produce a liquid biofuel (bio-oil) in a simple way and solid and gas fractions that can be used as energy sources to support the process. However, in order to incorporate bio-oils in current infrastructures and further processing in future biorefineries, their quality needs to be improved. Introducing different low-cost catalysts and/or incorporating different plastic residues to the process are some of the possibilities to achieve this aim in an economic way

MAIN OBJECTIVE

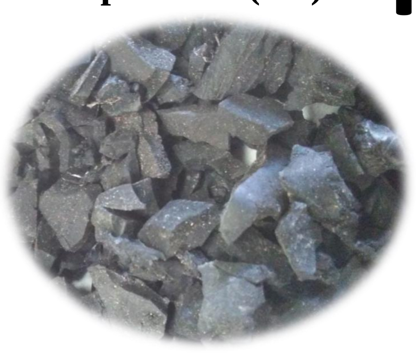
The implementation of new, simple and low-cost strategy through catalytic co-pyrolysis of grape seeds and waste tyres using CaO as a catalyst in a specifically designed fixed-bed reactor, that allows the user to directly obtain high quality bio-oils to be used as renewable energetic vector

FEEDSTOCK AND CATALYST

Table 1. Feedstock (grapes seeds and waste tyres) characterisation.

	Grapes seeds	Waste tyres
Ash	4.6	3.8
Volatile matter	69.5	63.6
Fixed Carbon	25.9	31.8
Ultimate analysis (wt. %)		
C	57.6	87.9
H	6.3	7.4
N	2.4	0.3
S	0.2	1.1
O	33.7	3.3
HHV (MJ/kg)	23.5	38.6
LHV (MJ/kg)	22.2	37.0

Grape Seeds (GS)



Waste Tyres (WT)

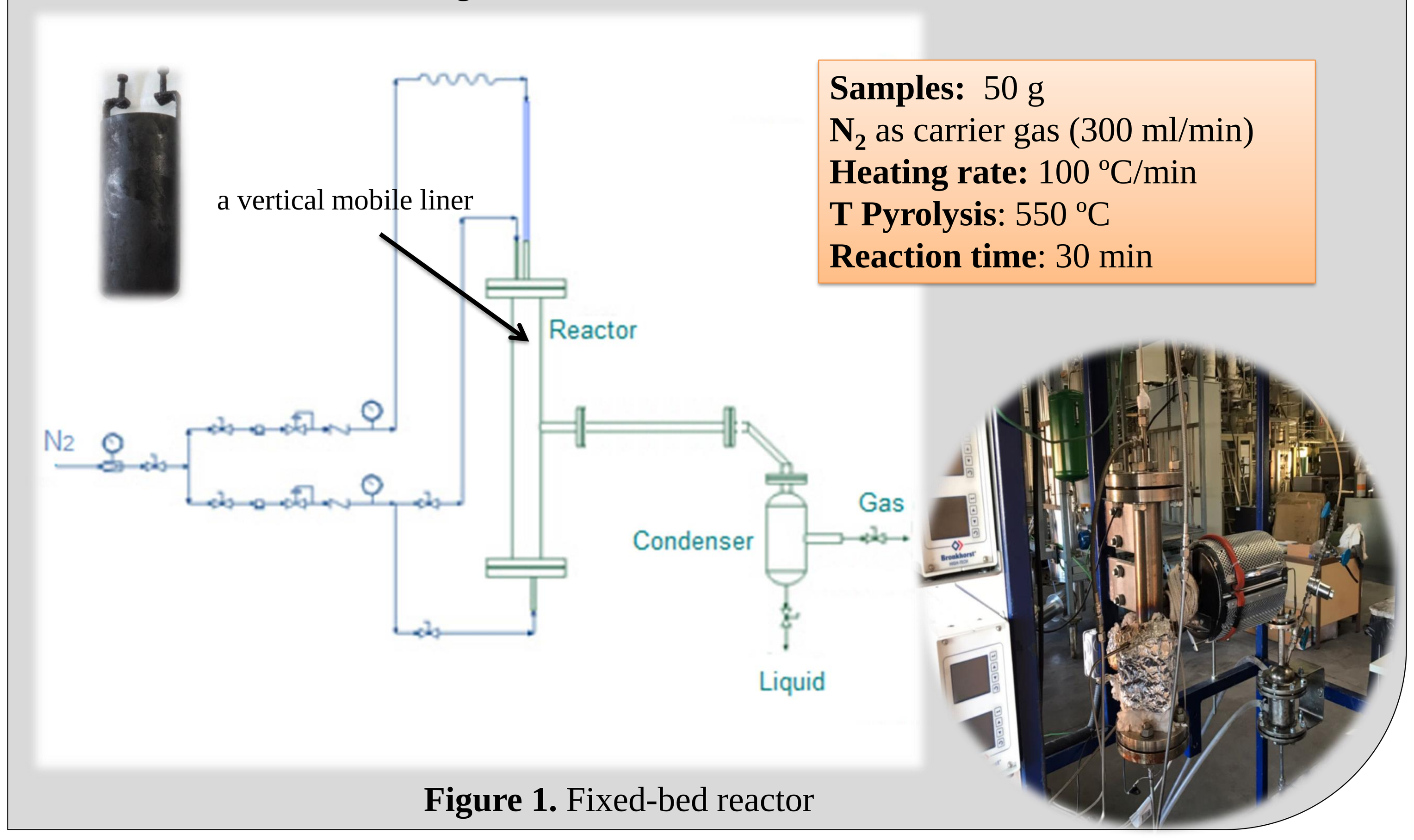
calcined calcite (CaO)

Different proportions of GS/WT in wt. % were studied:
95/5; 90/10; 80/20; 60/40
Keeping a ratio feedstock to CaO on 1:1

EXPERIMENTAL

FIXED-BED REACTOR

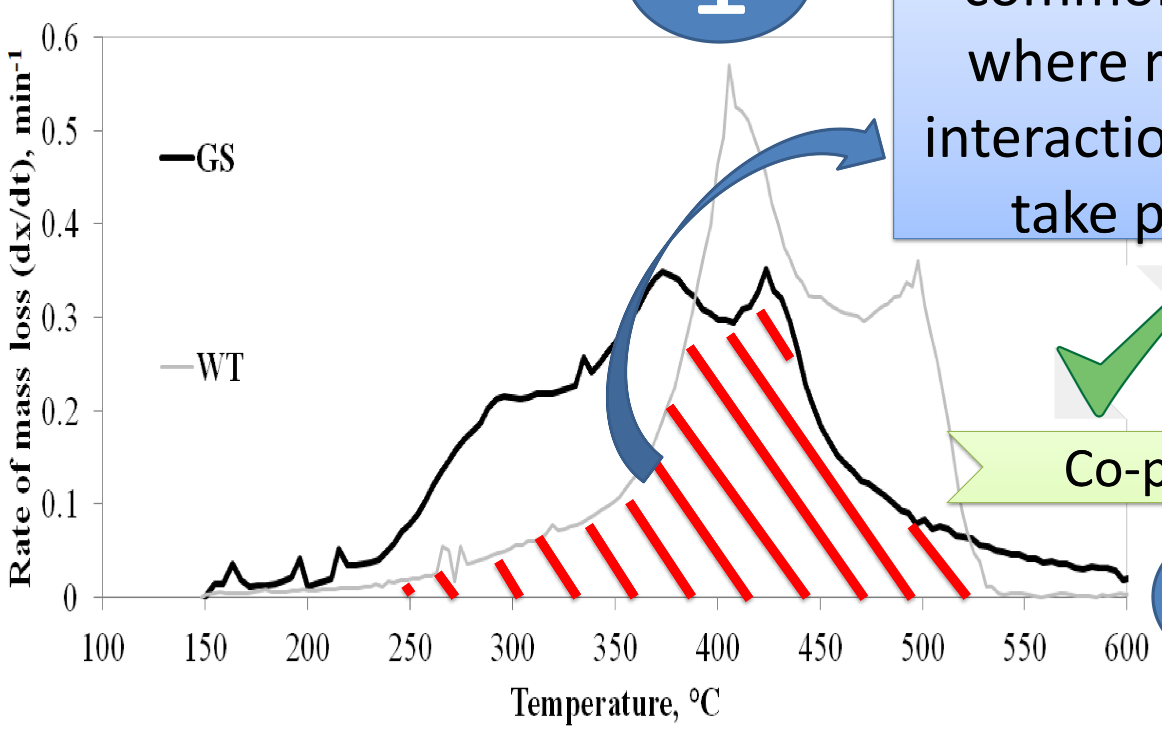
Stainless steel fixed bed reactor (52.5 cm length and 5 cm internal diameter). This reactor has designed specifically to carry out this process having the peculiarity incorporate a vertical mobile liner, where feedstock is deposited, A condenser (ice-cooled trap) using a water reflux at 3ºC was used to collect the gas condensable fraction



Samples: 50 g
N_2 as carrier gas (300 ml/min)
Heating rate: 100 ºC/min
T Pyrolysis: 550 ºC
Reaction time: 30 min

Figure 1. Fixed-bed reactor

RESULTS



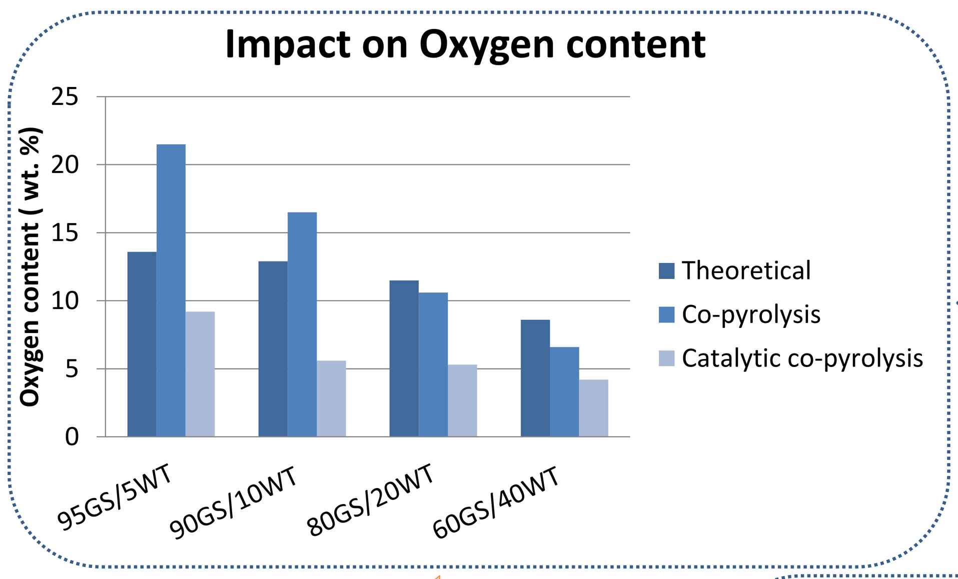
Significant common area where radical interaction could take place

Figure 2. TGA analysis at 100ºC/min

Table 2. Product yields in wt. % after conventional pyrolysis of GS and WT, co-pyrolysis of GS and WT and catalytic co-pyrolysis of GS and WT

Section	Experiment	Liquid			Solid	Gas
		Total	Org.	Aq.		
Conventional pyrolysis	GS	39.0	61.0	39.0	33.4	21.8
	WT	43.7	100.0	0.0	37.6	14.9
Co-pyrolysis of GS and WT (Theoretical values in brackets)	95GS/5WT	42.6 (39.2)	58.8 (62.9)	41.2 (37.1)	31.6 (33.6)	21.6 (27.2)
	90GS/10WT	42.5 (39.4)	69.8 (64.9)	30.2 (35.1)	31.6 (33.8)	21.9 (26.7)
	80GS/20WT	41.0 (39.9)	66.2 (68.8)	33.8 (31.2)	34.0 (34.2)	26.2 (25.8)
	60GS/40WT	42.2 (40.8)	77.4 (76.6)	22.6 (23.4)	33.8 (35.1)	20.0 (24.1)
Catalytic co-pyrolysis						
Keeping Feedstock/CaO ratio 1/1	95GS/5WT-CaO	44.0	56.3	43.7	40.0	12.1
	90GS/10WT-CaO	44.7	55.7	42.3	40.2	13.7
	80GS/20WT-CaO	43.8	57.7	47.3	40.2	15.6
	60GS/40WT-CaO	44.0	60.7	39.3	39.0	15.3

Synergetic effects on liquid yields (10 wt.% more than expected)



ORGANIC PHASE

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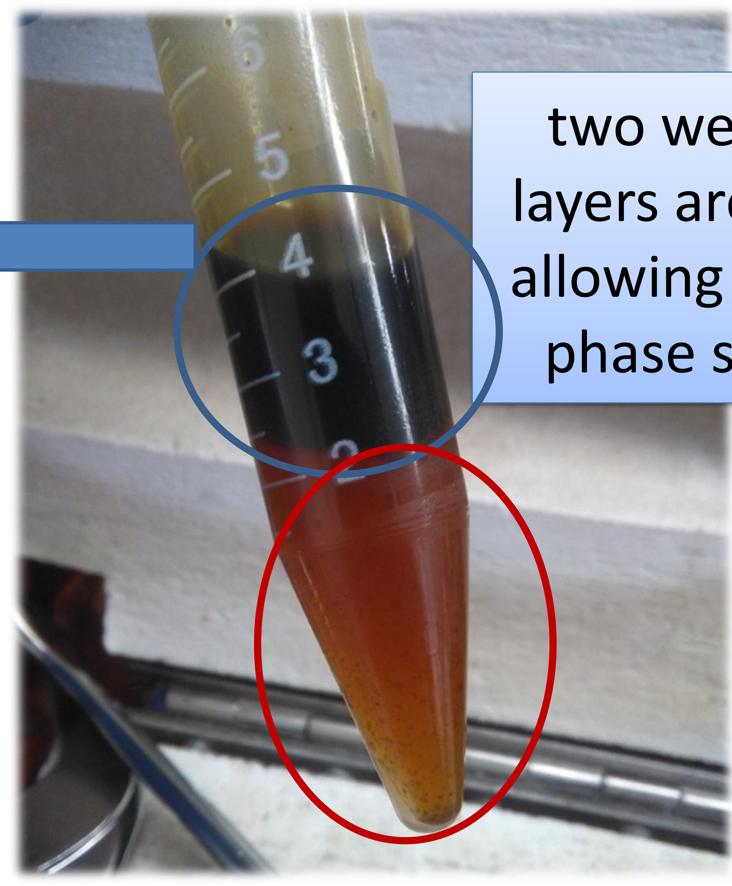

two well-defined layers are obtained, allowing for an easy phase separation

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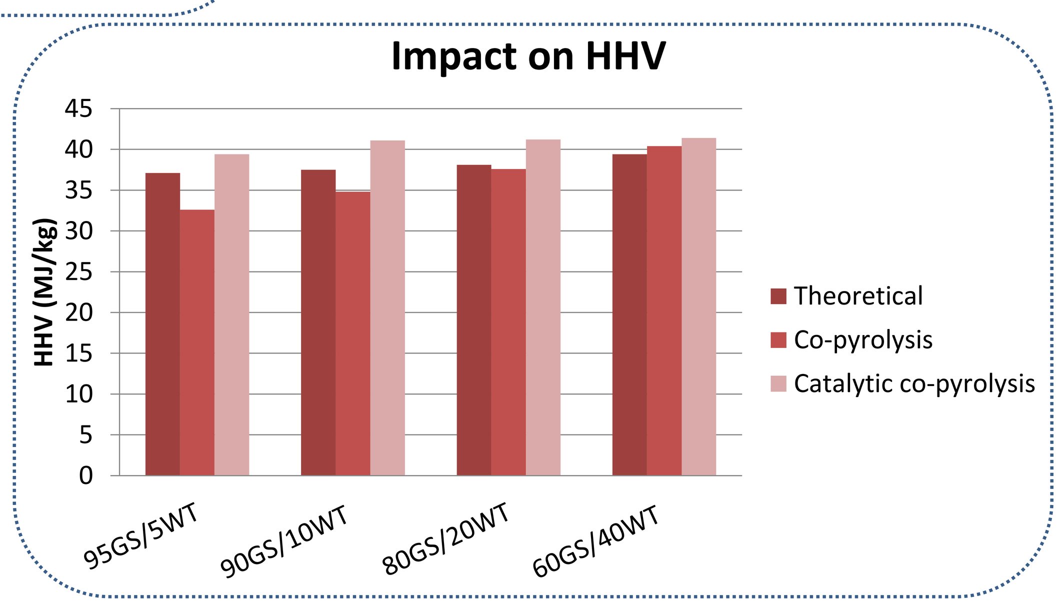
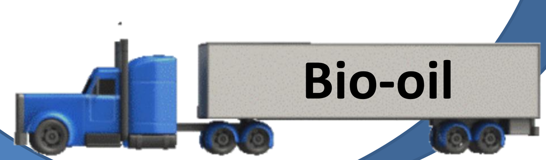
Figure 3. Bio-oil obtained from catalytic co-pyrolysis of GS and WT, using CaO as a catalyst (ratio 1 to 1 by weight)



A more deoxygenated and valuable bio-oil

To the bio-refinery



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CONCLUSSIONS

The results achieved show the great potential of GS to carry out the catalytic co-pyrolysis process with WT to produce a liquid bio-oil that can be considered as a high quality renewable vector. This liquid, more deoxygenated and with higher heating value, could be used as a feedstock in future bio-refineries and/or be processed jointly with fossil fuels in current refineries minimizing the adverse environmental impact due to fossil fuels use. Optimizing the operational conditions to maximize organic fraction yields and improving the organic fraction properties (optimizing feedstock-catalyst proportion in the feeding and analyzing catalyst lifetime after several regeneration cycles) are the next steps for the development of a new generation of bio-oils from catalytic co-pyrolysis of grape seeds and waste tyres using CaO as a catalyst

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