Role of the particle size on the yield of hazelnut shell pyrolysis products

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CREST
Catalytic Reaction Engineering for Sustainable Technologies

Naxos, Greece, 15th June 2018

Aim of the work

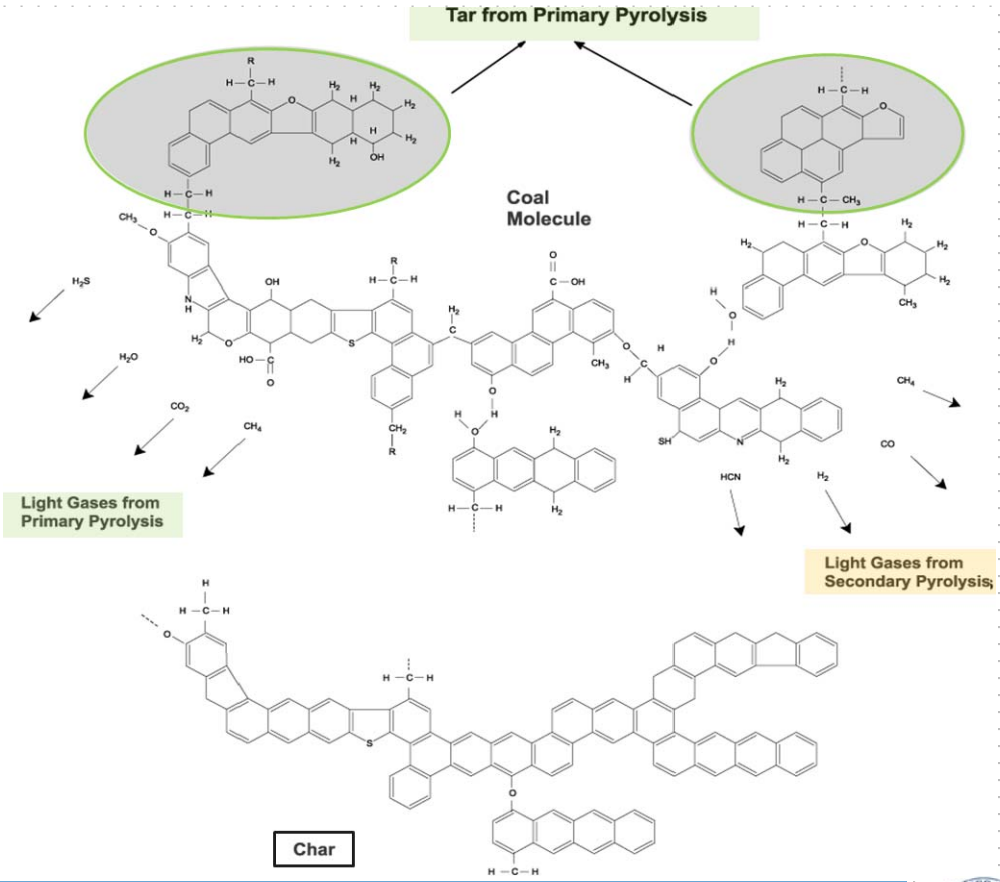
- Climate change imposes a radical change in the energy production for the *reduction of polluting air emissions*
- One way can be the switch from fossil fuels to ***biomass*** as alternative energy source
- Advantages: i) much less generation of air emissions; ii) reduction of waste to landfill; iii) reduction of dependence on foreign oil
- **Pyrolysis** is one of the most widely used methods to convert residual biomass into valuable fuels
- This research aims at promoting the *environmental and energetic sustainability* of the hazelnut chain industry in the Piedmont Region (northern Italy)
- The objective of this study was to investigate the ***effect of biomass particle size*** on products yield of hazelnut shell pyrolysis, especially on gas production yield, at *different heating rates*
- This research tries to expand the understanding of the pyrolysis of the hazelnut shells and the *influence of the process parameters on the obtained products*, in the perspective of identifying the most suitable conditions for obtaining the highest energy and gas production yields

Pyrolysis process

Pyrolysis is the thermal decomposition of organic materials in the absence of oxygen

Parameters:

- chemical and structural composition
- particle size and species of the used biomass
- temperature
- heating rate
- humidity
- residence time

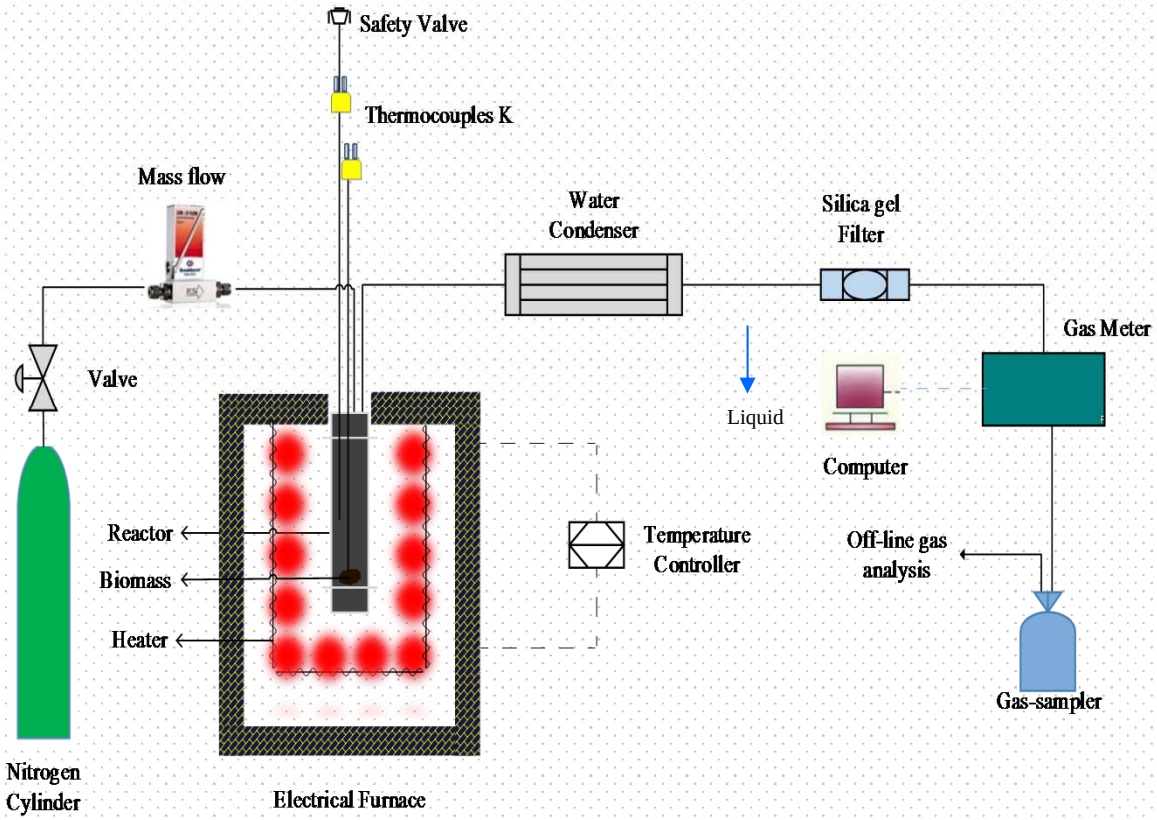


Materials and methods

- Feedstock: hazelnut shells generated during the processing of hazelnuts
- HS = hazelnut shell with "original dimensions" (0.5 cm)
- HSM = average size of 100 µm obtained by a milling process for 30 min
- Composition, ultimate and proximate analyses by ASTM standards (E871, D1102-84)
- HHV by bomb calorimeter
- Thermogravimetric analysis up to 800 °C in Ar atmosphere using three heating rates (6, 12 and 30 °C/min)

Analysis	Hazelnut Shells (Feedstock)
Ultimate analysis (dry, wt.%)	
C (%)	55.1
H (%)	6.3
N (%)	1.6
O (by difference) (%)	37
Proximate analysis (wt.%)	
Moisture (% p/p)	5.3
Volatile matter	77.1
Fixed carbon	21.1
Ash (%)	1.8
Composition of lignocellulosic material (wt.%)	
Cellulose	30.5
Hemicellulose	25.9
Lignin	35.1
HHV (MJ/Kg)	18.8
pH	5.3

Pyrolysis experimental setup



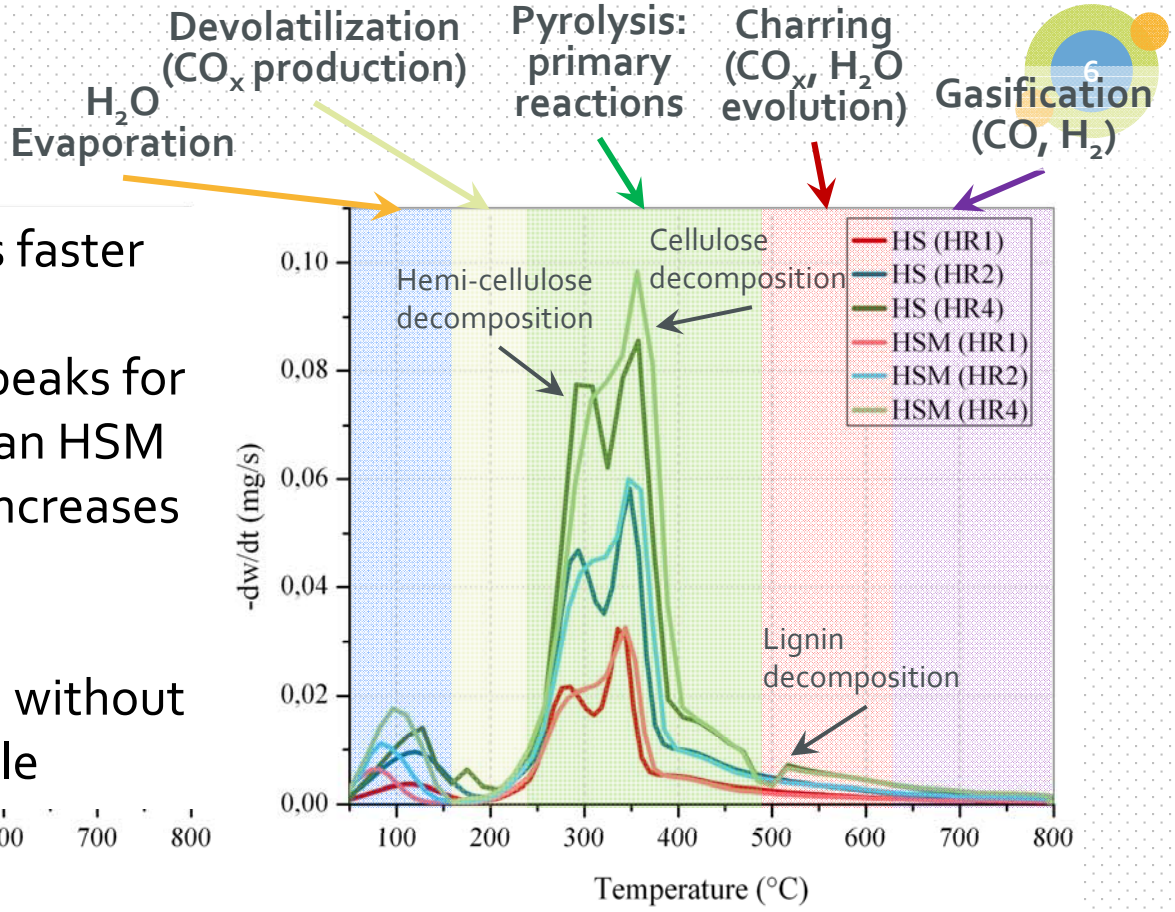
Pyrolysis experiments

- Final temperature: 800 °C
- Four different heating rates: 6 (HR1), 12 (HR2), 20 (HR3) and 30 (HR4) °C/min

- Procedure:
  - Condenser and reactor flushed with nitrogen (100 ml/min) for 30 minutes to remove air from the system
  - Total amount of biomass used in each experiment: 3 g
  - After each test, liquid, gas and solid phases recovered for off-line analysis
  - Chemical analysis of the gas phase performed by SRA Micro GC equipped with TCD attached directly to the sampling point.

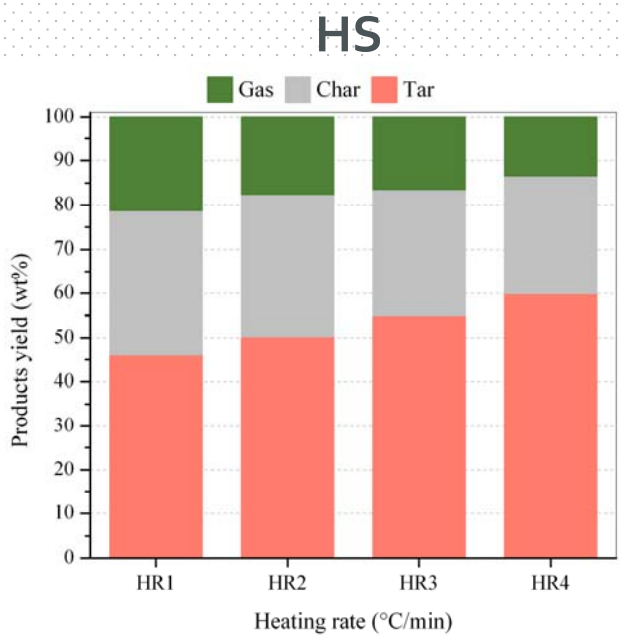
Results: TGA tests

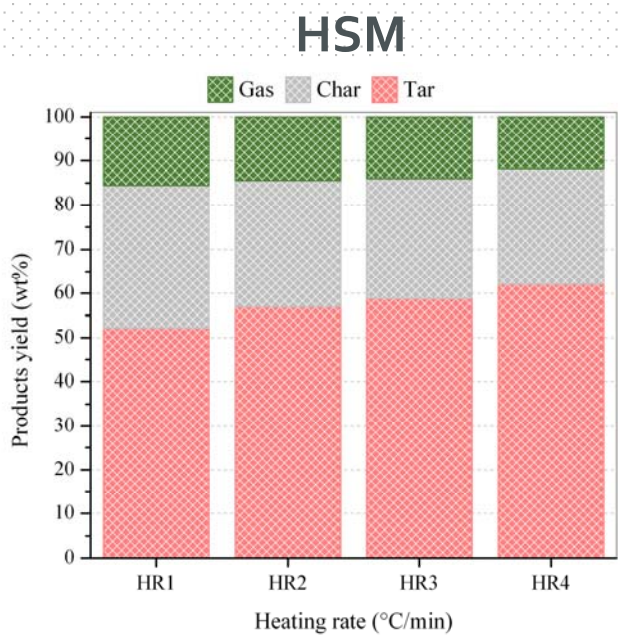
- First stage: HSM weight loss faster than HS
- Second stage: 2 significant peaks for mass loss, sharper for HS than HSM
- Maximum weight loss rate increases by increasing HR
- HR increase only shifts peak temperature to higher value without change decomposition profile



Results: gas, char and tar yields

- HR increase → increase of tar yield, decrease of gas and char yields
- Effect of particle size is inversely proportional to HR
- Tar yield for HS is lower than HSM at the same HR
  - Smaller particles have low mass transport resistance to vapours, released quickly before secondary cracking
- Gas yield for HSM is slightly lower than HS

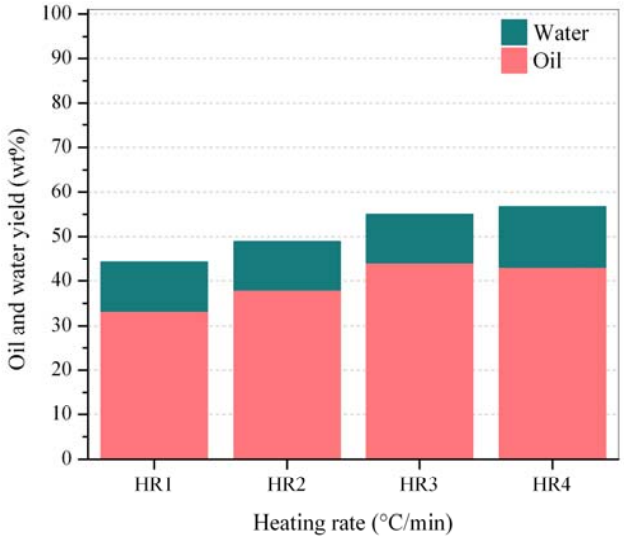




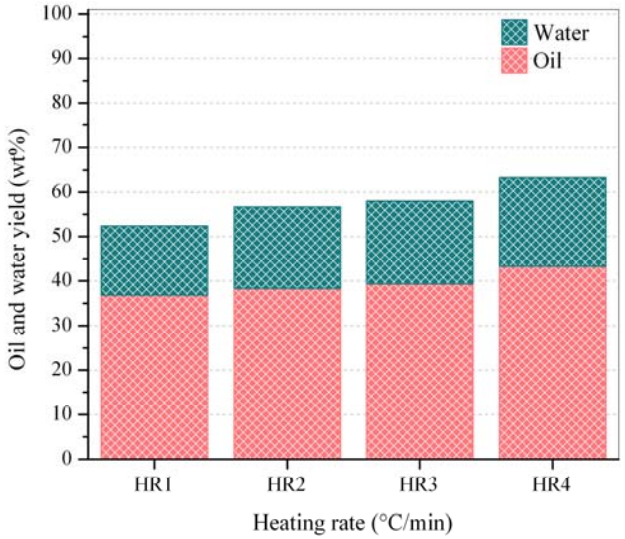
Results: tar water content

- Very high water content at lower particle size
- Water/oil ratio almost constant with different HR (slight water increase by HR increase)
- HSM: higher heat transfer rate → higher localized T →secondary fraction reactions

HS

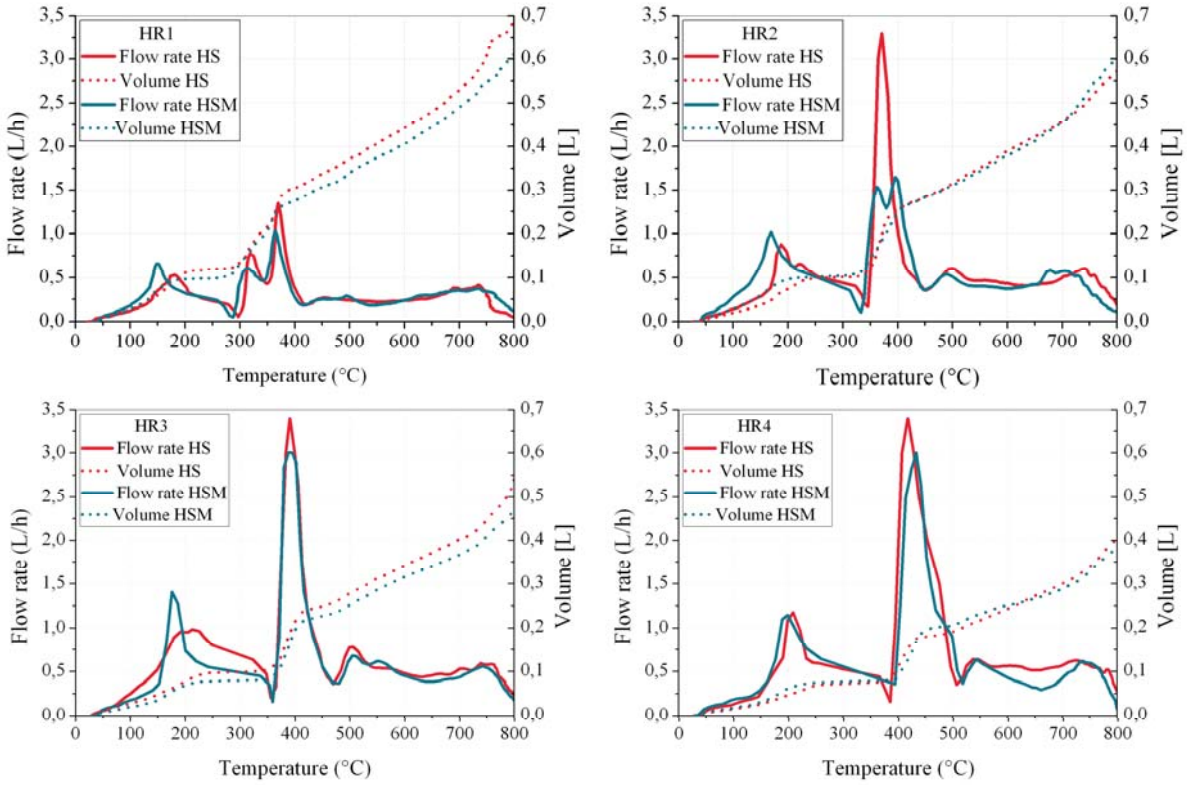


HSM



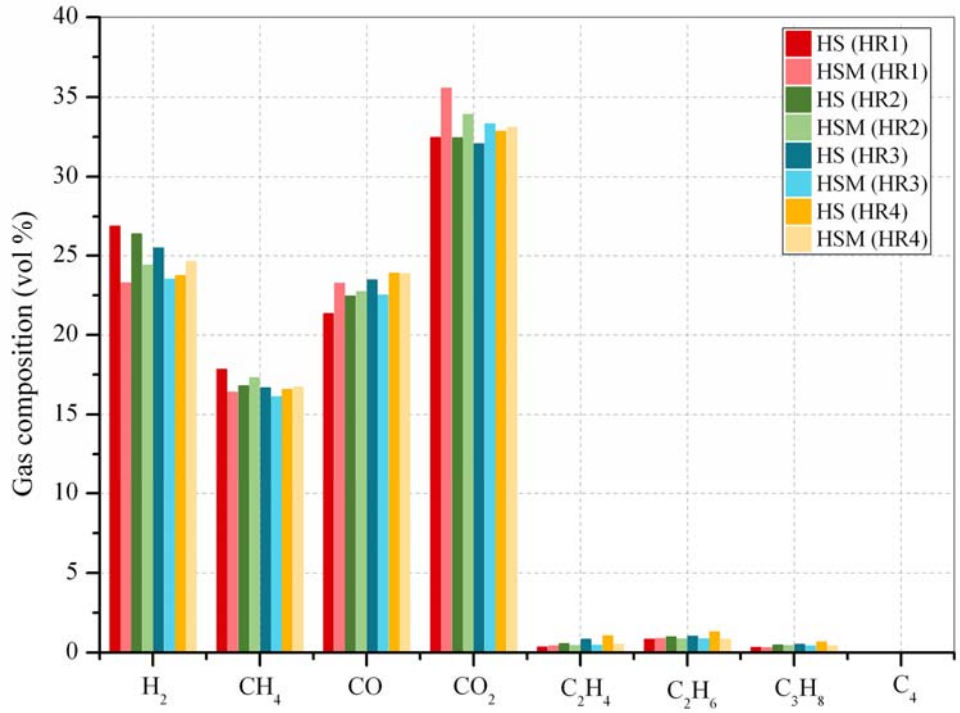
Results: gas production

- TGA results confirmed
- 3 steps:
  - I) drying up to 130 °C
  - II) pyrolytic cracking 130-500 °C
  - III) lignin degradation over 500 °C
- HR increase ⇨ only shift upward of peak temperatures, thermal profile of decomposition maintained
- HR increase ⇨ increase of maximum rate of decomposition



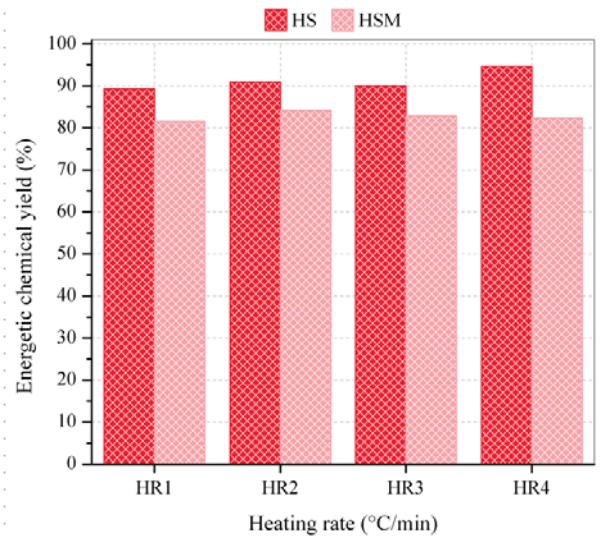
Results: gas composition

- CH_4 from decomposition of methoxy, methyl, and methylene groups
- CO_2 from decarboxylation reaction and the breakage of carbonyl groups
- CO from breakage of ether bonds and C=O bonds
- No significant differences in gas composition between HS and HSM
- HS favours the H_2 formation
- HR increase ⇨ increase of C_2 and C_3 gases (thermal degradation of the lower long chain organic vapors)



Results: char, tar and gas HHV

		HS	HSM
Char [MJ/kg]	HR1	31.38	28.33
	HR2	30.30	31.13
	HR3	30.29	30.34
	HR4	30.24	28.99
Tar [MJ/kg]	HR1	15.02	14.49
	HR2	14.14	14.65
	HR3	13.84	14.34
	HR4	14.41	14.21
Gas [MJ/kg]	HR1	12.61	12.23
	HR2	13.41	12.60
	HR3	13.30	12.18
	HR4	15.11	12.64



- Similar HHV values of pyrolysis products for HS and HSM
- Highest HHV for char
- HS produces higher energetic chemical yield than HSM at same HR (higher amount of char produced)

Conclusions

- The effect of particle size on the pyrolysis of hazelnut shell was studied
- The *increase of heating rates only shifts upward the peak temperature* without changing thermal profile of decomposition
- By *manipulation of the biomass particle size* in pyrolysis reactions, it is possible to have some *influence on the products yield*
  - Particle size decrease (milling) causes **tar yield increase** (up to 62.1%), **bio-oil water content increase** and **gas yield slight decrease**
  - **Energetic chemical yield** is higher for larger particle size
  - *Gas composition is not affected* by change in particle size
- From the point of view of the energy content and gas yield, **the particle reduction is not economically convenient** (the pretreatment increases costs without improvement in yields)
- These results demonstrate that *optimization of pyrolysis parameters* (particle size, temperature, HR) can be useful for larger/commercial pyrolysis to reduce costs, simplify process and create high energy content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