In situ catalytic upgrading of pyrolysis oils from beech wood with calcium-based catalysts

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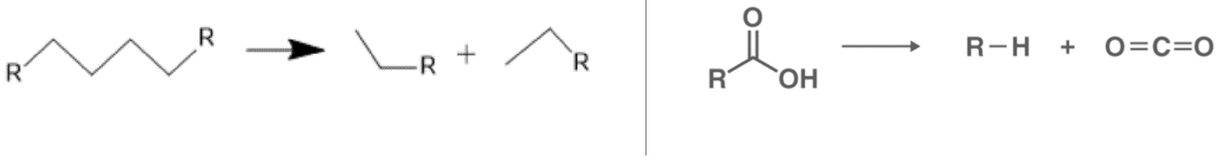
Introduction 1

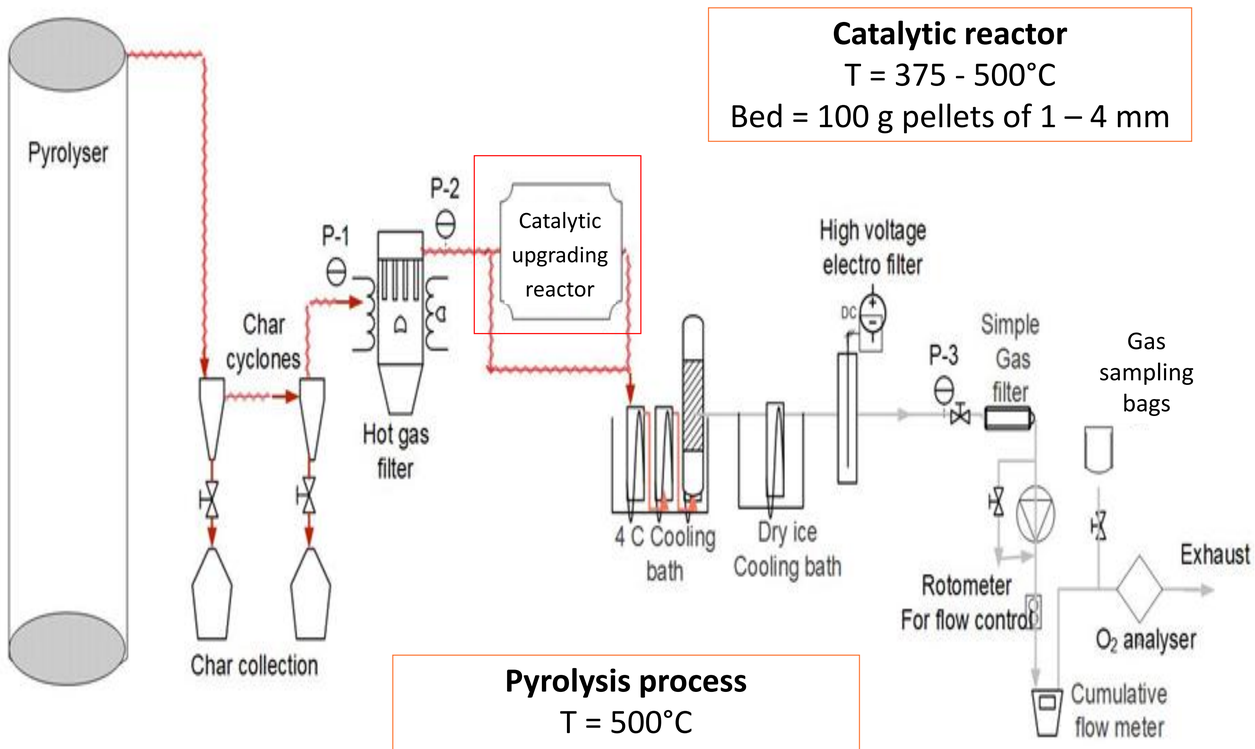
The marine industry contributes a substantial share to the worldwide CO_2 emissions, which is expected to grow over the next decades [1].

Fast pyrolysis of biomass or plastic waste can produce a biocrude with a high water and oxygen content, leading to high acidity, low storage stability and low energy density [2]. Fast pyrolysis of plastics leads to a waxy product with long chain hydrocarbons.



Calcium-based solids from the cement industry like cement raw meal (CRM) and calcined cement raw meal (cCRM) with high amounts of $CaCO_3$ and CaO respectively, can be used as low-cost catalytic materials in the conversion of oxygen containing molecules, as well as basic cracking catalysts for reducing the waxy character of oils as shown in the above reactions.

Methods 2



Catalytic reactor
T = 375 - 500°C
Bed = 100 g pellets of 1 – 4 mm

Pyrolysis process
T = 500°C
t = 4 sec
Feeding rate = 0.5 kg/h
Fluidized bed = 700 g Sand
Fluidizing agent = Nitrogen gas

Condition	Density [g/cm³]	Nitrogen [ppm]	Sulfur [ppm]
Base case	1,11	844	72
CRM 500	1,09	890	44
cCRM 375	1,11	1650	114
cCRM 500	1,10	2022	152
ZSM5 375	1,12	1393	122
ZSM 5 500	1,10	807	134

Table 1: Properties relevant for a application as shipping fuel . Density, sulfur and nitrogen content.

Results 3

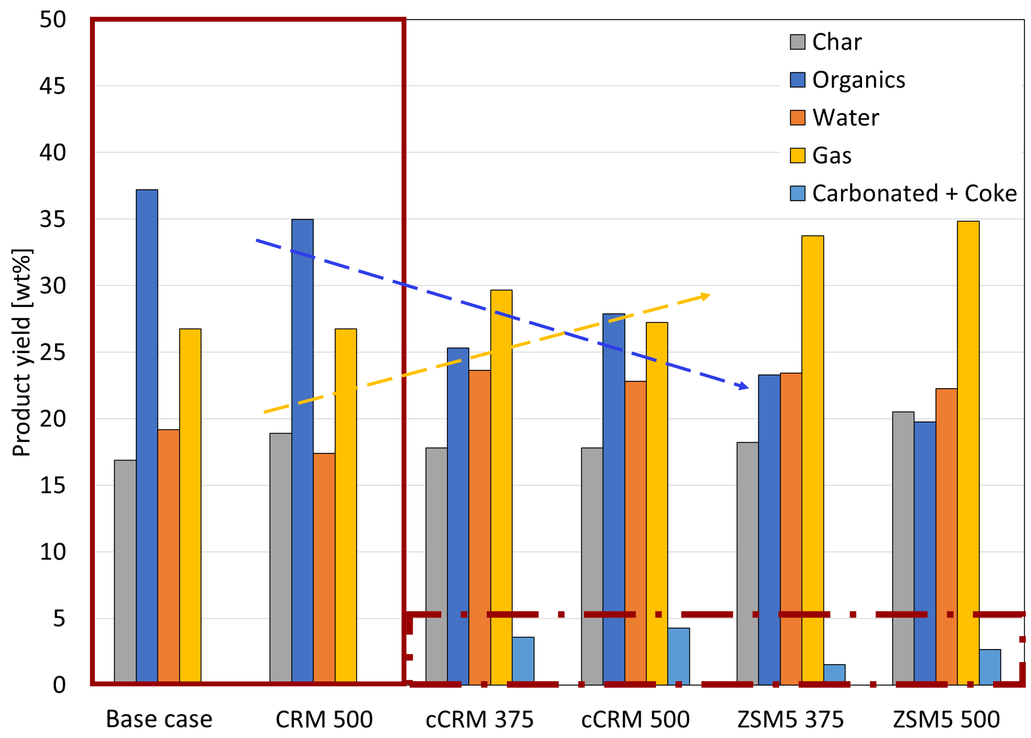


Figure 1: Product yield, collected from pyrolysis with different materials (CRM= Cement raw meal; cCRM=calcined cement raw meal; ZSM5= H-ZSM-5 zeolite) at temperatures 375 or 500 °C in upgrading reactor. Base case is without catalytic upgrading reactor.

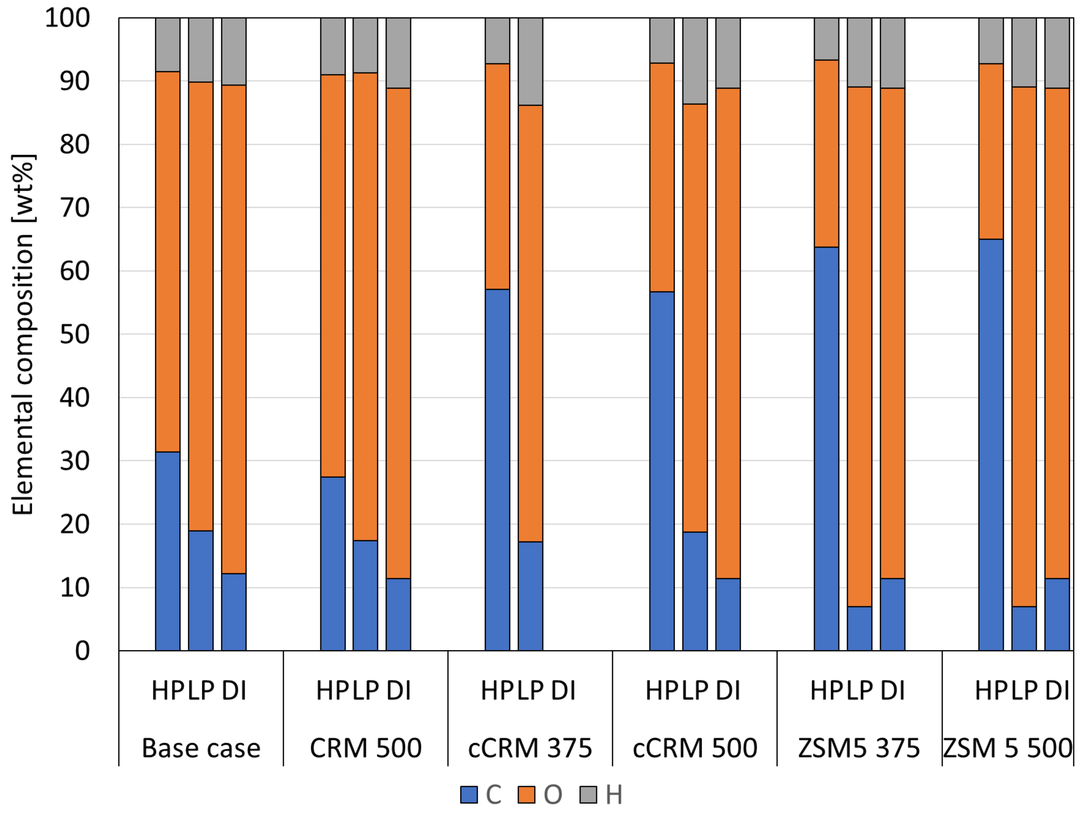


Figure 2: Elemental composition of the liquid products (HP=heavy phase; LP= light phase; DI=dry ice).

Conclusion 4

- **The organic phase yield decreased and the gas yield increased** with higher temperature in the reactor and stronger basicity/acidity of the catalyst
- Calcined raw meal deactivated through coking and especially **recarbonation**
- The sulfur and nitrogen content increased through **upconcentration in the heavy phase** over upgrading**.** The density was mostly unaffected
- The elemental composition of heavy phase strongly shifted towards **more carbon and less oxygen with catalytic treatment**.
- Overall **calcined cement raw meal showed similar performance as H-ZSM5**

[1] Dabros, T. et al; Progress in Energy and Combustion Science, 2018, 68, 268-309. [2] Veses, A. et al; Bioresource Technology, 2014, 162, 250-258. [3] Eschenbacher, A. et al.; Energy Fuels, 2019, 33, 6405–6420.

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