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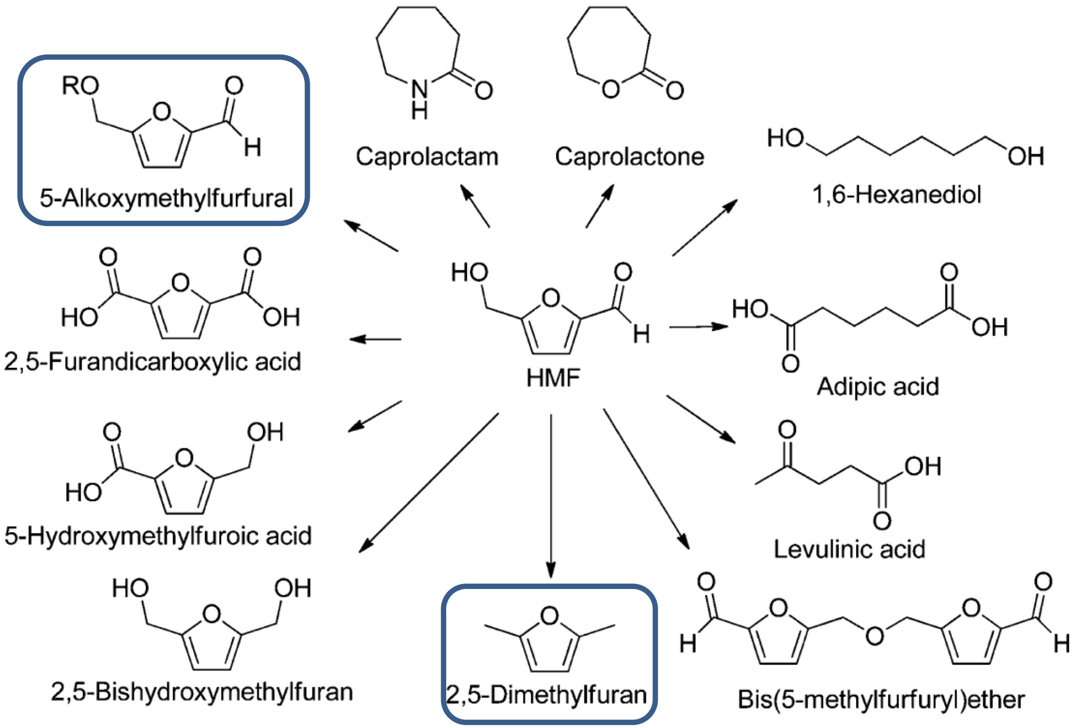
WP4 Progress 29-6-2016

WP4

- Partners: ECN, AVT
- 41 PM, Month 1-48.
- Goals:
  - Developing thermochemical conversion routes of seaweed fractions and isolated sugars to furan-based fuels.
  - Upscaling to kg scale and production of fuel for engine tests.

Why furans?



RO
O
O
H
5-Alkoxymethylfurfural
N
H
O
Caprolactam
O
O
Caprolactone
HO
OH
1,6-Hexanediol
O
O
O
HO
OH
2,5-Furandicarboxylic acid
HO
O
O
H
HMF
HO
O
OH
O
Adipic acid
O
OH
O
HO
5-Hydroxymethylfuroic acid
O
OH
O
Levulinic acid
HO
OH
O
2,5-Bishydroxymethylfuran
O
2,5-Dimethylfuran
O
O
O
O
O
H
H
Bis(5-methylfurfuryl)ether

Approach

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- Research on furan-based fuels production from
    1. Alginate (uronic acids, brown seaweeds) → furfural
    2. Xylose (red & green seaweeds) → furfural
    3. Laminarin (glucose, brown seaweeds) → hydroxymethylfurfural (HMF)
    4. Rhamnose (green seaweeds) → 5-methyl furfural
- Production of sufficient fuel for characterisation (WP5)
- Production of one fuel for engine test (WP5)

Approach & Deliverables

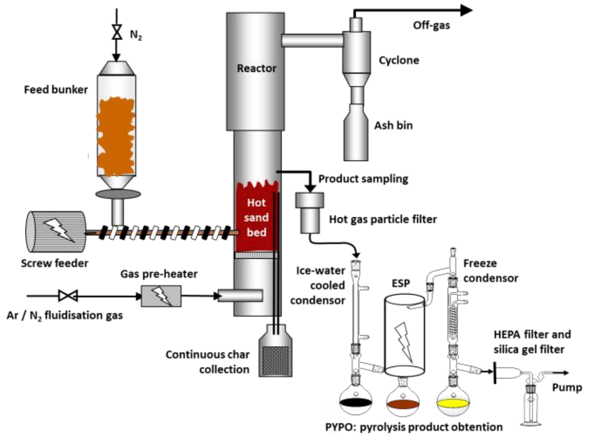
Deliverable	Title	Partner(s)	Due date
D4.1	Alginate based furanic fuel	ECN	24
D4.2	Xylose based furanic fuel	AVT, ECN	30
D4.3	Laminarin / glucose based furanic fuel	AVT	30
D4.4	Rhamnose based furanic fuel	ECN	30
D4.5	Fuels sample for WP5 for engine testing	ECN, AVT	36

- Focus AVT: organic solvent-based conversion.
- Focus ECN: aqueous (4.2 and 4.4) and solvent-free (4.1) approaches.

4.1 Alginate to furfural (ECN)

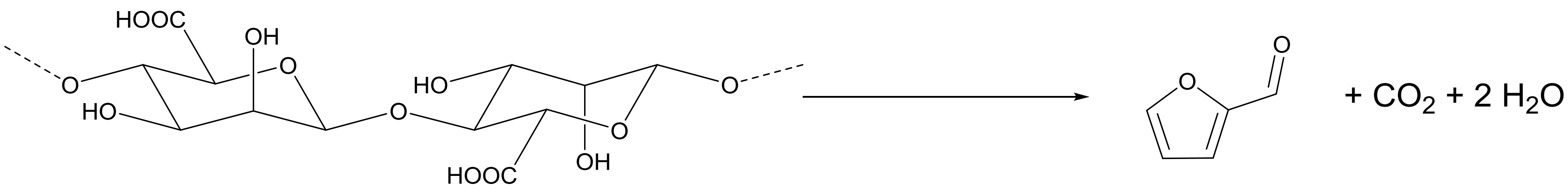
- Starting point:
  - Literature.
  - Analytical Py-GC/MS work in earlier project on alginic acid showing selective formation of furfural.

Analytical Py-GC/MS



Fluidized bed reactor

4.1: Reaction



Alginic Acid

furfural

- $(C_6H_8O_6)n \rightarrow C_5H_4O_2 + CO_2 + 2H_2O$
- Theoretical mass yields: 54.5 wt% furfural, 25% CO_2 and 20.5 wt% H_2O.

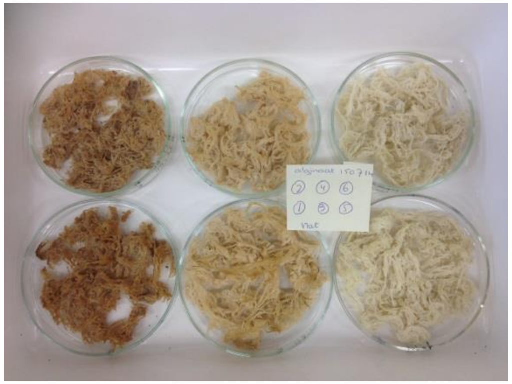
4.1 Alginate to furfural

- Benefit:
  - Easier separation of furfural compared to current water-based processes (diluted streams, azeotrope).
- Viable route?
  - Not based on current pure and expensive alginate sources.
  - However, giant reduction of alginate price expected when large-scale seaweed biorefinery is implemented.
  - Research questions:
    - Can we use impure alginate streams (further cost reduction)?
    - Can we scale-up from mg-scale to kg-scale?

4.1: Alginate to furfural

- Approach:
  - Commercial alginic acid conversion using analytical Py-GC/MS → optimum conditions.
  - Conversion of commercial alginic acid to furfural on kg-scale using bench-scale (fluidized bed) pyrolysis equipment.
  - Production of fuel for initial fuel analysis (WP5).
  - Verification of route using alignic acid isolated from seaweed (WP2).

Laminaria digitata



Isolated alginate

4.1 Py-GC/MS screening

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- Literature study:
  - Temperature > 200 °C required.
  - Wide temperature range applicable: 200-700 °C.
  - Max yield @300 °C.
  - > 400 °C increase in side-products.

- Py-GC/MS:
  - Highly selective furfural production from alginic acid
    - Main side products: 2,3-butanedione, acetone & acetic acid in addition to various furans.
  - Not from Na- or Ca-alginate.
  - Temperature screened from 200-550 °C. Results largely in-line with literature:
    - T of at least 250 °C required.
    - No large differences observed in furfural yield > 300 °C.
    - Optimum seems ~350 °C.
  - Quantification of results with internal standard ongoing.

4.1 Fluidized-bed pyrolysis

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- Three tests performed:
  - ~1 kg/hr fluidized-bed pyrolysis reactor (hot sand, three stage product condensation).
  - 300, 350 and 400 °C.
  - Feed: 200 gr commercially obtained alginic acid (extruded at ECN).
- 350 and 400 °C: experiment had to be stopped due to agglomeration of bed, probably due to melting of alginic acid.
- Test at 300 °C succesful with respect to feeding, but low yield.

Experiments

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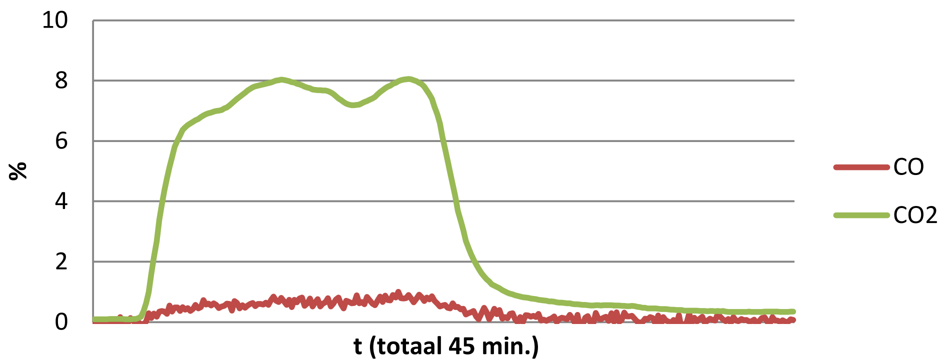
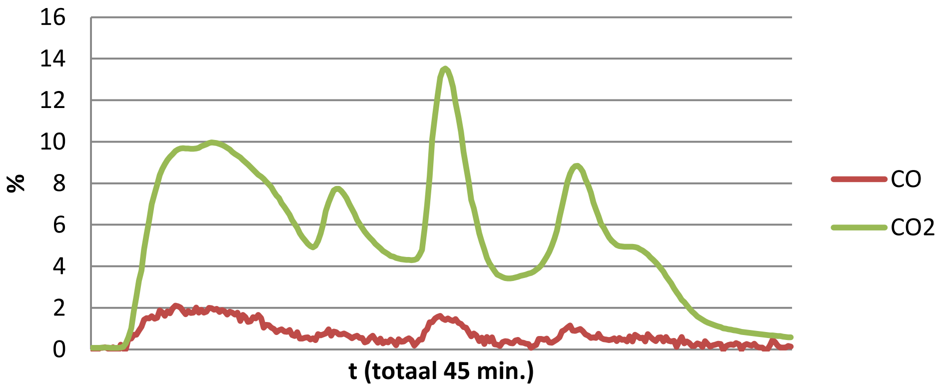
300C

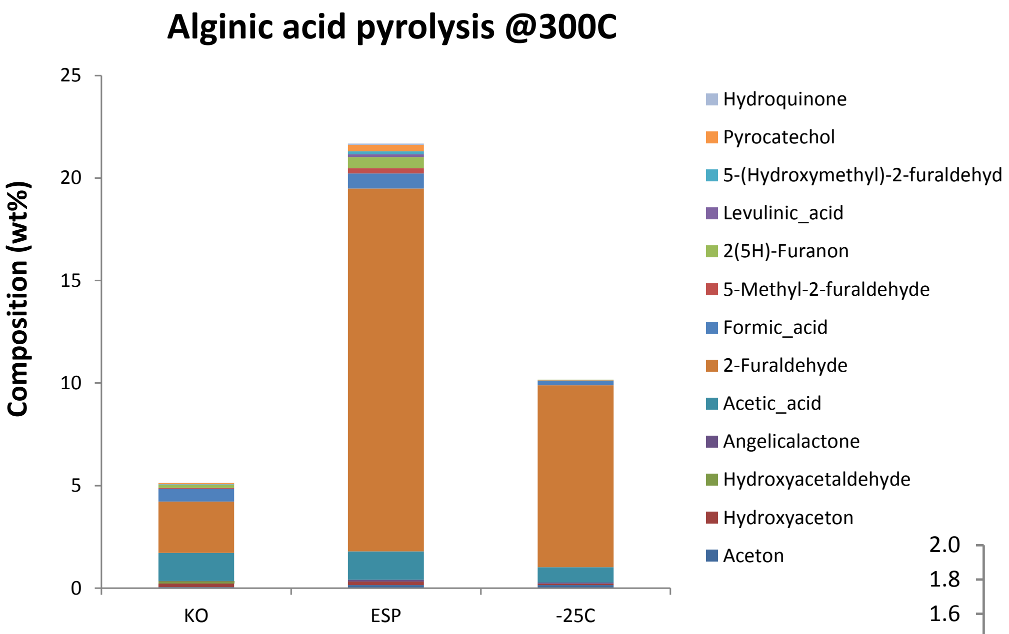


400C



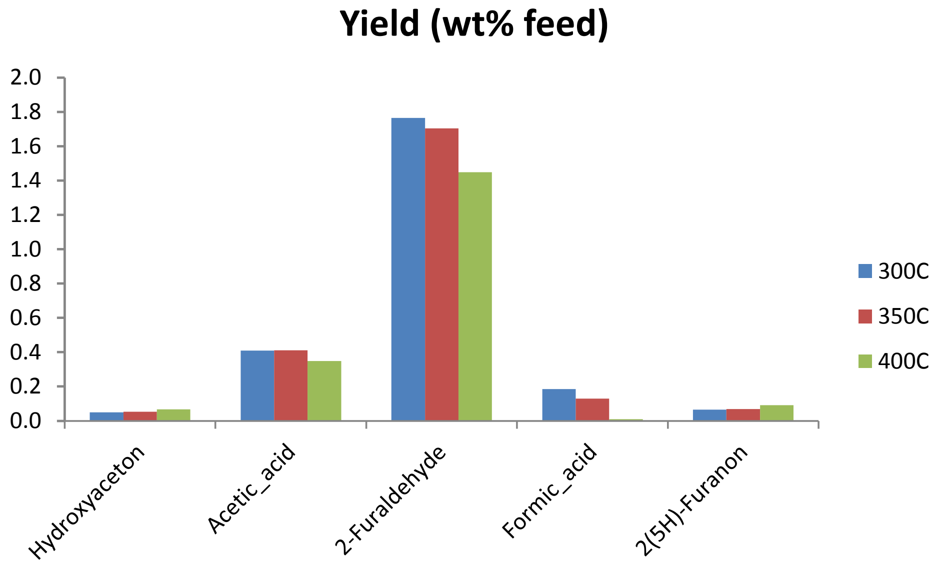
400C: bed agglomeration

Yields



Composition:

- KO and -25: rest is H_2O.
- ESP: 43 wt% organic unknowns (probably oligomers)



Mass balances:

- Closed (95%).
- Near theoretical yield of CO_2.
- Higher than theoretical yield of H_2O.
- Polymerisation of furfural?
- Future tests: reducing solid residue.

4.2: Xylose to furfural (AVT, ECN)

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- Approach:
  - Benchmark condition xylose conversion to furfural: literature study and experimental verification.
  - Application of determined conditions for conversion of xylose-rich streams from WP2 to produce furfural-based fuel for WP5.

Palmaria palmata

4.2: Status

- ECN:
  - No experimental work performed yet.
  - Literature study on aqueous conversion of pentoses to furfural ongoing.
  - Inventory and determination of composition of macroalgae (including pentoses) ongoing in WP2.

Tasks

- 4.2: Furfural from C5 sugar feeds
  - No work has been done on this

4.3: Glucose to furans (AVT)

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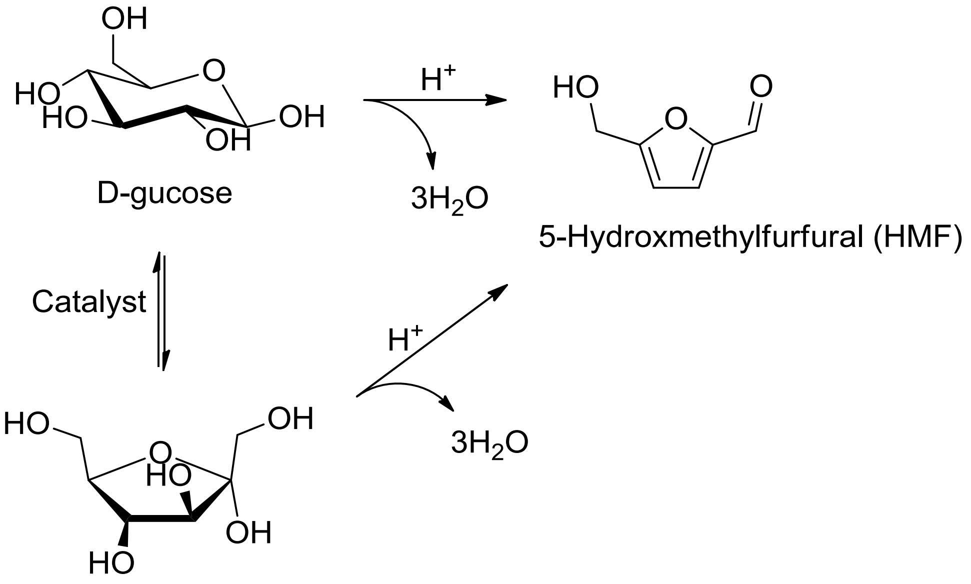
- Approach:
  - Starting point: AVT process for production of furanics from starch / glucose.
  - Isomerisation of glucose in laminarin hydrolysates from WP2 to fructose
  - Application of AVT process for conversion to furans
  - Production of a suitable amount of fuel for tests in WP5.

Tasks

- 4.3: Conversion of laminaran to furans
  - We’ve performed some experiments in the last few weeks

Sugars to furans

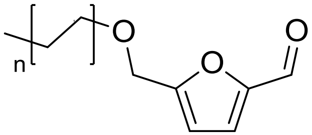
- Dehydration



- Yields:
  - From glucose: ~5%
  - From fructose: 40-90%, depending on the method

Conversion of laminaran to furans

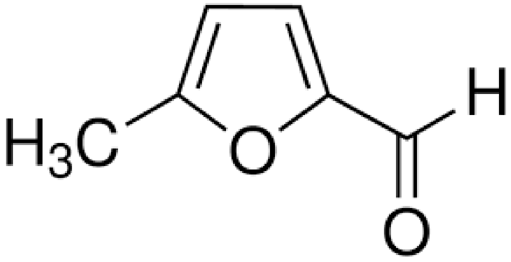
- Laminaran is a polymer of glucose
  - Requires multi-step process to form HMF
    - Hydrolysis
    - Isomerisation
    - Separation fructose and glucose
    - Dehydration of fructose
      - This is performed in alcohols
        - Forms an alkylated product for fuel



4.4: Rhamnose to 5-methyl furfural

- Starting point: rhamnose from Ulva succesfully converted to 5-methyl furfural by ECN in 2015.
- Approach:
  - Yield optimisation of process using commercial rhamnose.
  - Application optimum conditions for rhamnose (-rich streams) from Ulva in WP2.
  - Production of fuel for WP5.

Ulva sp.



4.4: Status

- ECN:
  - No experimental work performed yet.
  - Literature study on aqueous dehydration of rhamnose ongoing.
  - Inventory and determination of rhamnose content Ulva ongoing in WP2.

4.5: Fuel batch for engine testing

- Assessment together with WP5 on fuel properties determined in tasks 4.1-4.4.
- Selection of most promising fuel.
- Production of large fuel batch for engine tests in WP5 (10% blend, 20L biofuel).

- No activities yet.

Acknowledgement

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