Biorefinery I: Chemicals and Materials From Thermo-Chemical Biomass Conversion and Related Processes

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Pure aromatics from biomass

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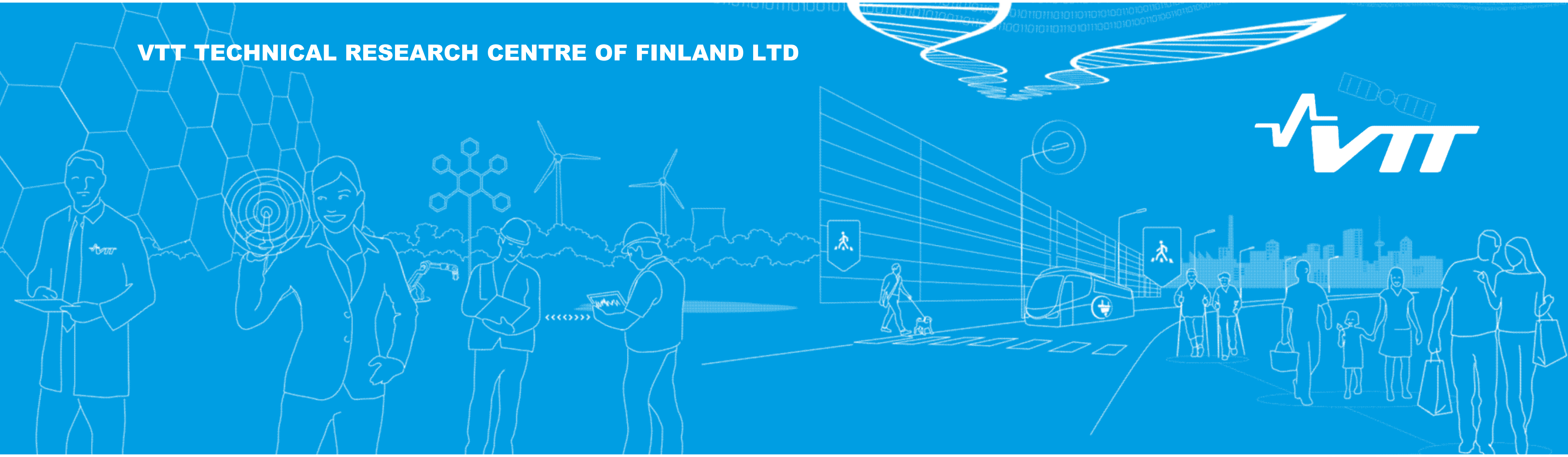

Pure aromatics from biomass

Biorefinery I: Chemicals and Materials From Thermo-Chemical Biomass Conversion and Related Processes

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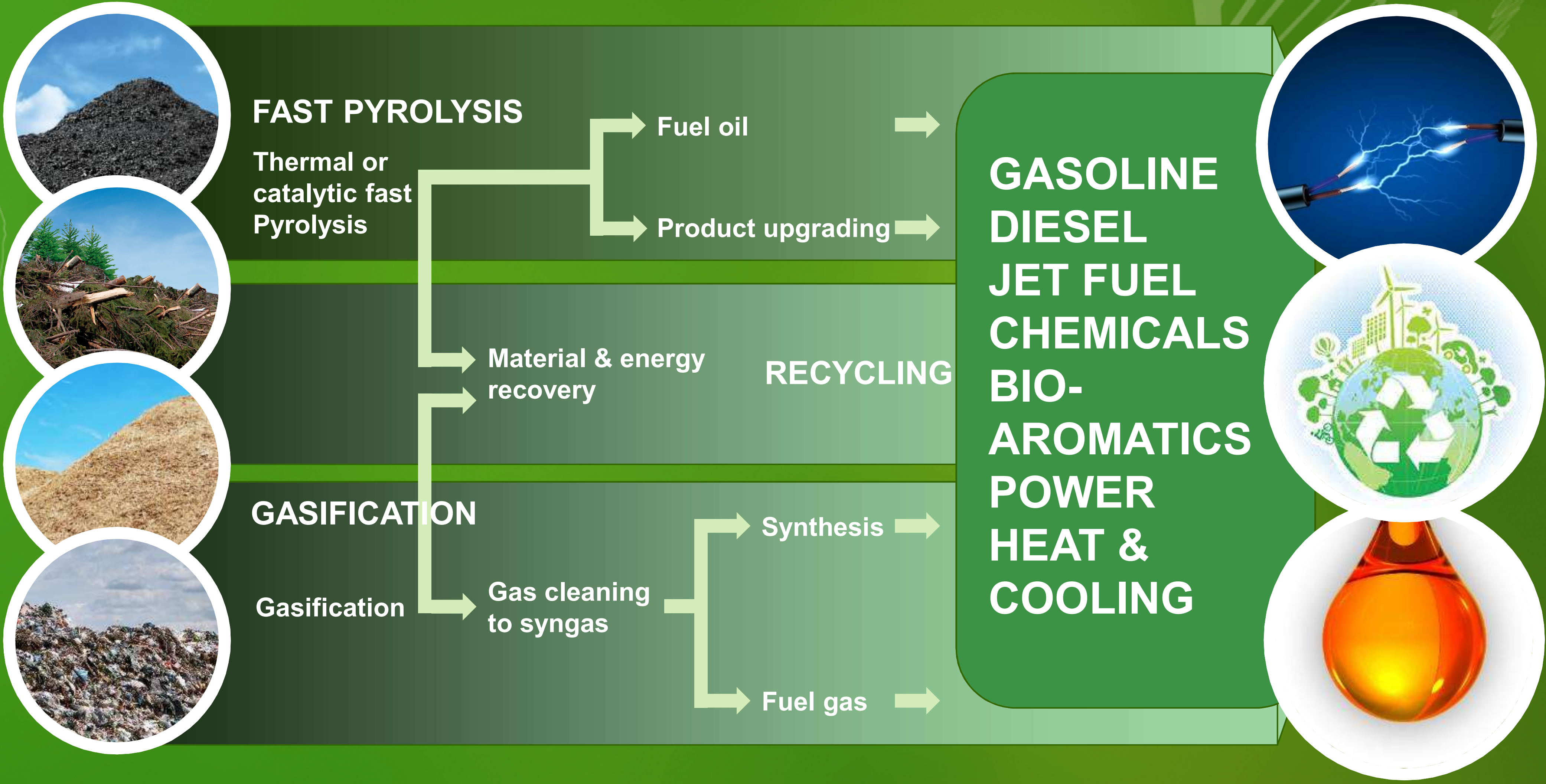
Outline

- Background /introduction
  - Why BTX via biomass gasification ?
  - Description of the process
- Laboratory scale experiments
  - Catalysts and reactor system
  - Product distribution, and separation of pure compounds
  - Example of a synthesis of an end-product
- Cost estimates for large scale production
- Next steps
- Conclusions

Thermochemical conversion: High-value products, low carbon energy and material recycling via thermochemical conversion



FAST PYROLYSIS

Thermal or
catalytic fast
Pyrolysis

Fuel oil

Product upgrading

Material & energy
recovery

RECYCLING

GASIFICATION

Gasification

Gas cleaning
to syngas

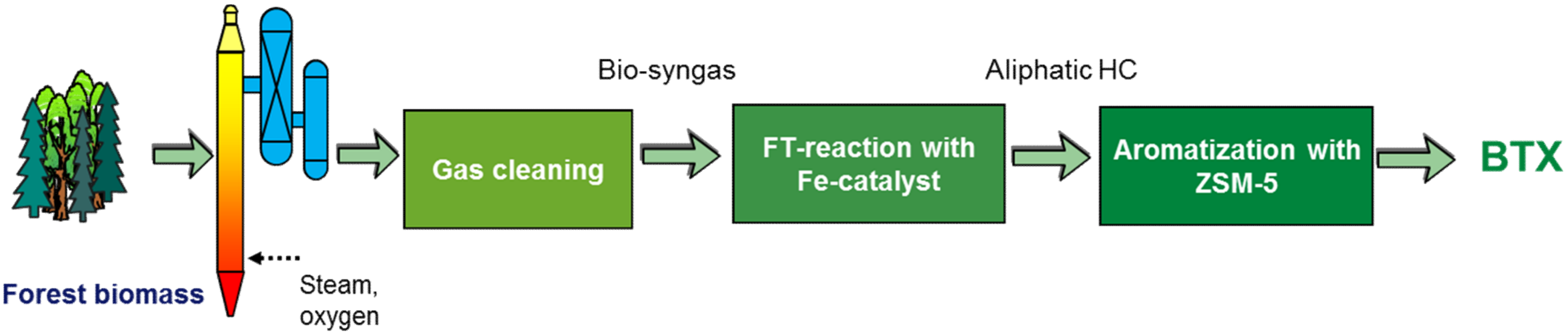
Synthesis

Fuel gas

GASOLINE
DIESEL
JET FUEL
CHEMICALS
BIO-
AROMATICS
POWER
HEAT &
COOLING

Biomass gasification route to BTX-chemicals

- BTL-process to diesel has been succesfully demonstrated. However, there aren’t any commercial plants
- As an alternative, we propose a cheaper process to valuable aromatic chemicals
- Competing technologies such as catalytic pyrolysis often suffer from bad selectivity – a mixture of phenols, methoxyphenols and substituted aromatics is of little value as a starting material for syntheses
- Principle of the process:



Forest biomass

Steam, oxygen

Gas cleaning

Bio-syngas

FT-reaction with Fe-catalyst

Aliphatic HC

Aromatization with ZSM-5

BTX

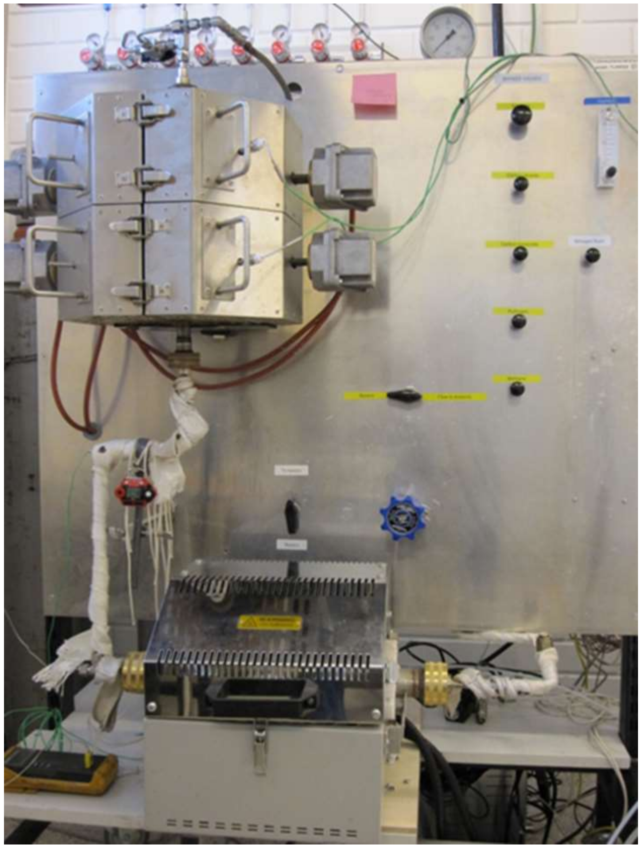
Laboratory scale experiments

A two-stage process:

a) Fischer-Tropsch-reaction over precipitated iron catalyst 100Fe:4.6Si:2.0Cu:1.4K (atom ratio)[1]. H_2/CO =1.4 mol/mol. Temperature 200 – 300°C, pressure 0.1 – 0.5 MPa.

b) Aromatization over ZSM-5 promoted by Zn (0.6 %) and La (0.8 %). Temperature 400 – 500°C, pressure 0.1 MPa.

Simple tubular reactors connected directly in series, on-line GC-analysis



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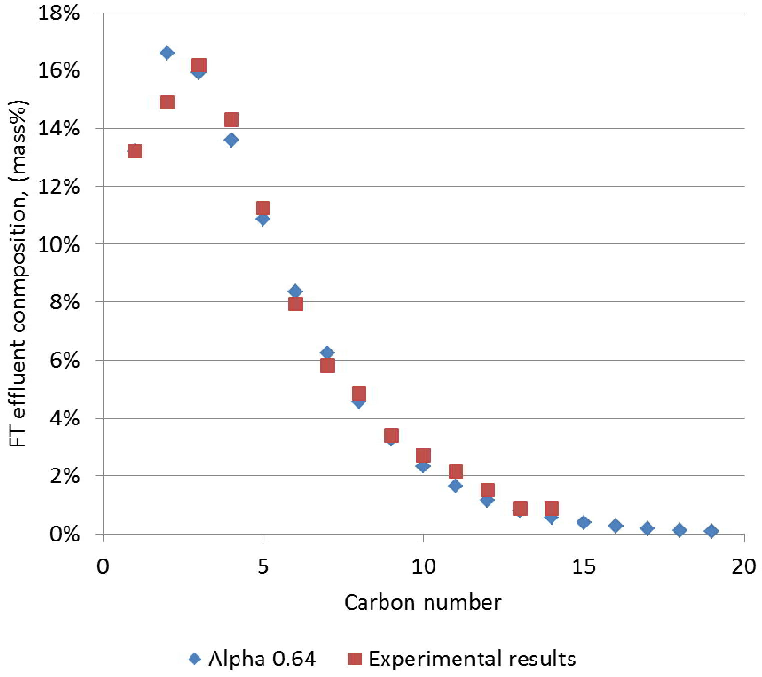
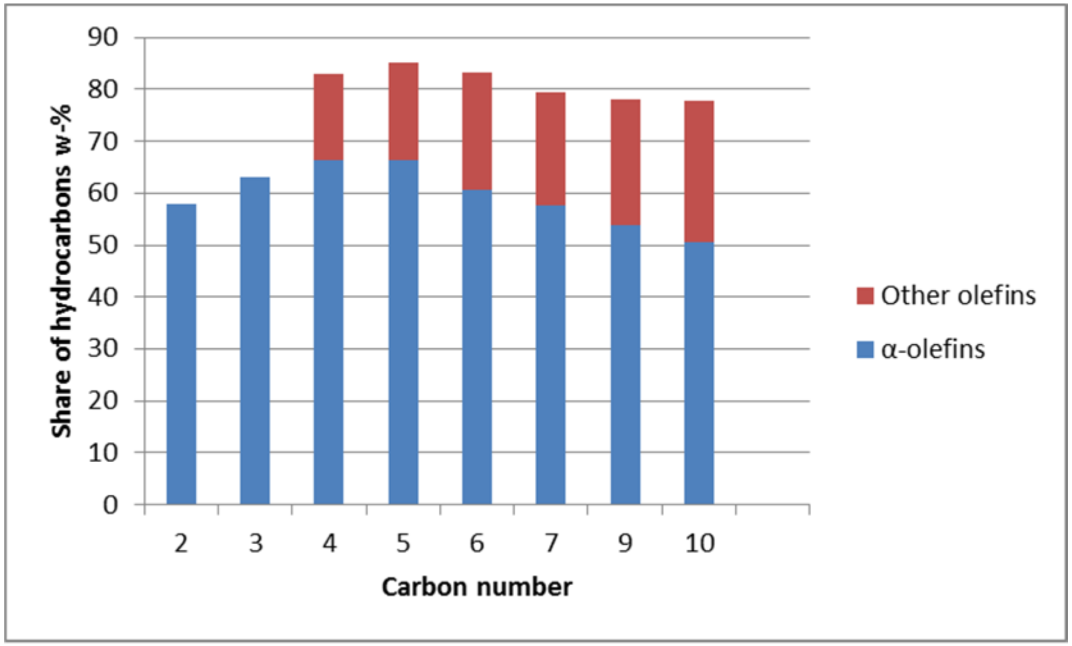
[1] Catal. Lett. (2013) 143, 1123-1131

[2] Chi. J. Chem. Eng. (2011) 19,439-445

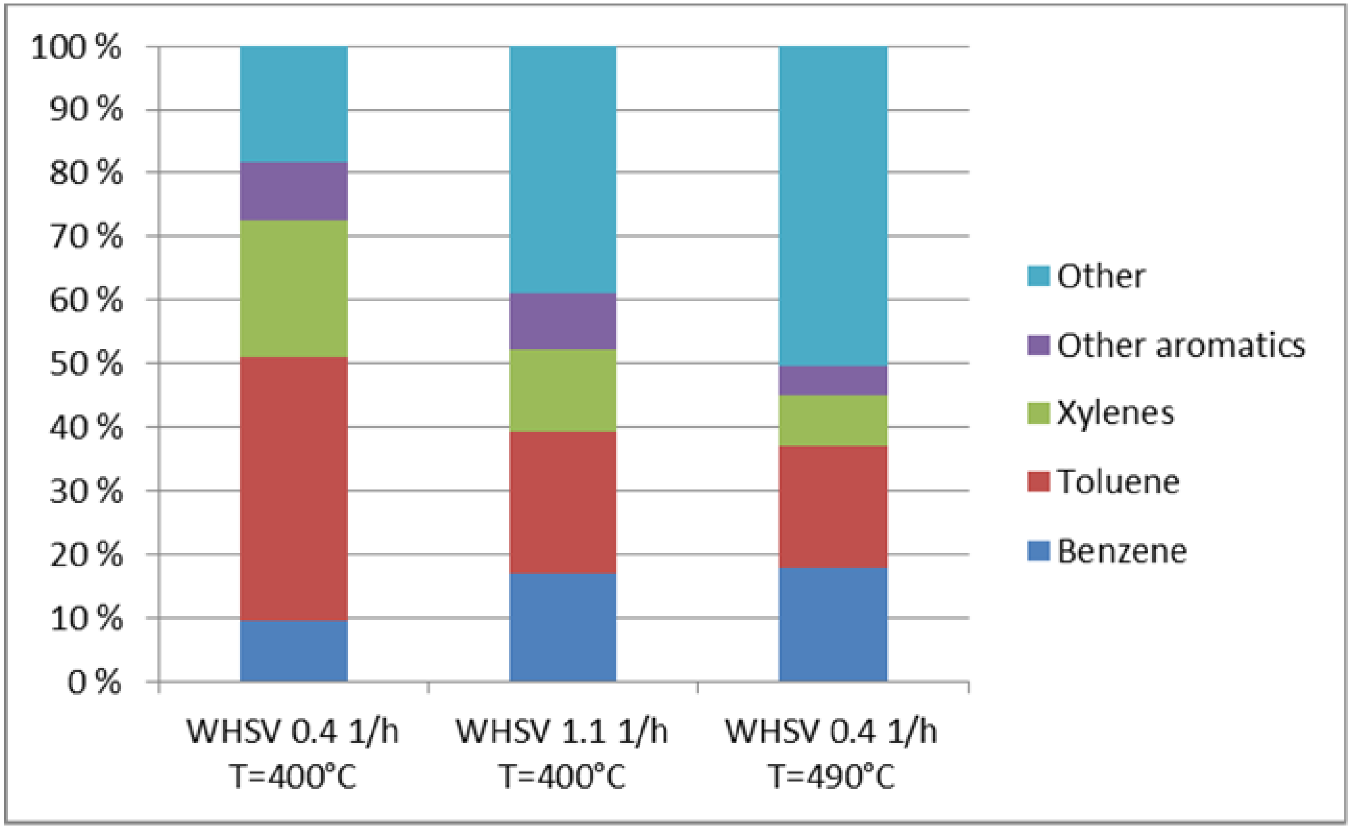
Step 1: FT reaction





FT-reaction step: H_2/CO=1.4 (mol/mol), 240°C, 0.1 MPa, WHSV=1.3 1/h, α=0.64, CO conversion 64 %

Step 2: The effect of aromatization conditions



FT-reaction step: H_2/CO=1.4 (mol/mol), 240°C, 0.1 MPa, WHSV=1.3 h^{-1}, α=0.64.

Composition of the reaction product (w-%)

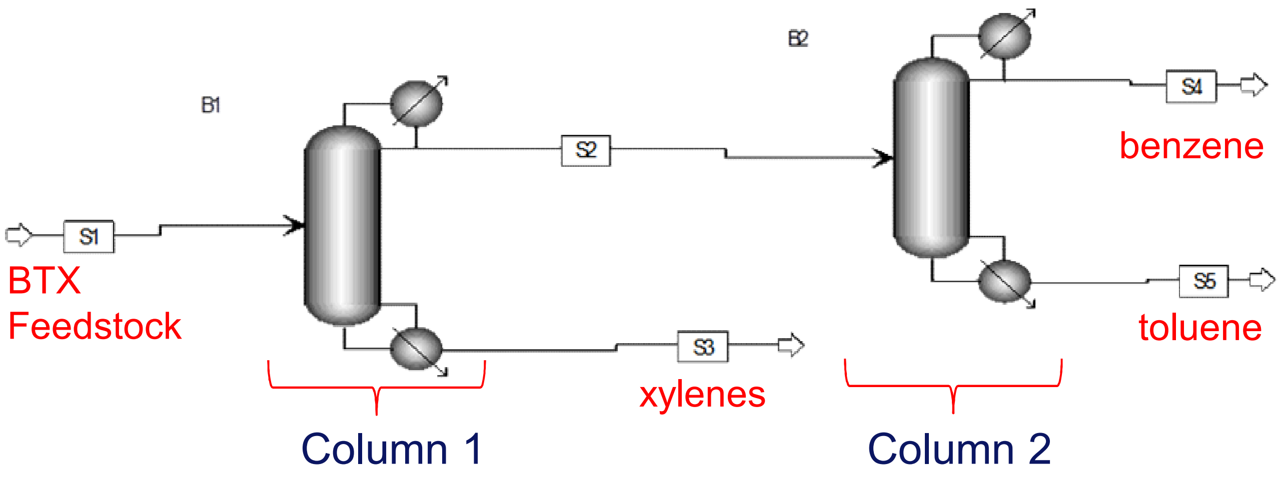
Product	WHSV 0.4 h^{-1} T=400°C	WHSV 1.1 h^{-1} T=400°C	WHSV 0.4 h^{-1} T=490°C
CO_2	2.6	4.2	6.9
CH_4	11.4	8.3	11.1
C2	2.9	16.2	19.2
C3	0.7	5.4	8.1
C4	0.5	4.1	4.2
C5	0.1	0.5	0.5
C6	0.0	0.1	0.3
Benzene	9.4	17.1	18.0
Toluene	41.5	22.2	19.0
Xylenes	21.5	13.0	8.0
C3-Benzene	8.6	7.2	3.7
C4-Benzene	0.4	0.7	0.3
Naphthalene	0.3	0.8	0.8
Methylnaphthalene	0.0	0.2	0.0
Dimethylnaphthalene	0.0	0.0	0.0
Total aromatics	81.8	61.2	49.8

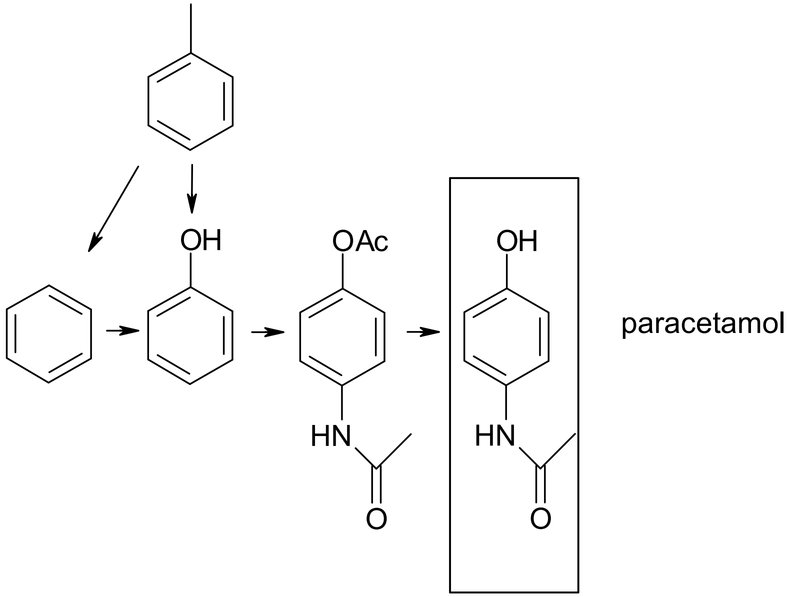
FT-reaction step: H_2/CO=1.4 mol/mol, 240°C, 0.1 MPa, WHSV=1.3 h^{-1}, α=0.64

Isolation of pure compounds for synthesis

- In large scale, according to ASPEN-modelling, a two distillation column set-up produces almost **pure benzene and toluene** fractions.
- In laboratory BTX-compounds were separated using Vigreux distillation followed by crystallisation

- As an example of synthesis, bio-paracetamol was synthesised from the separated benzene and toluene fractions





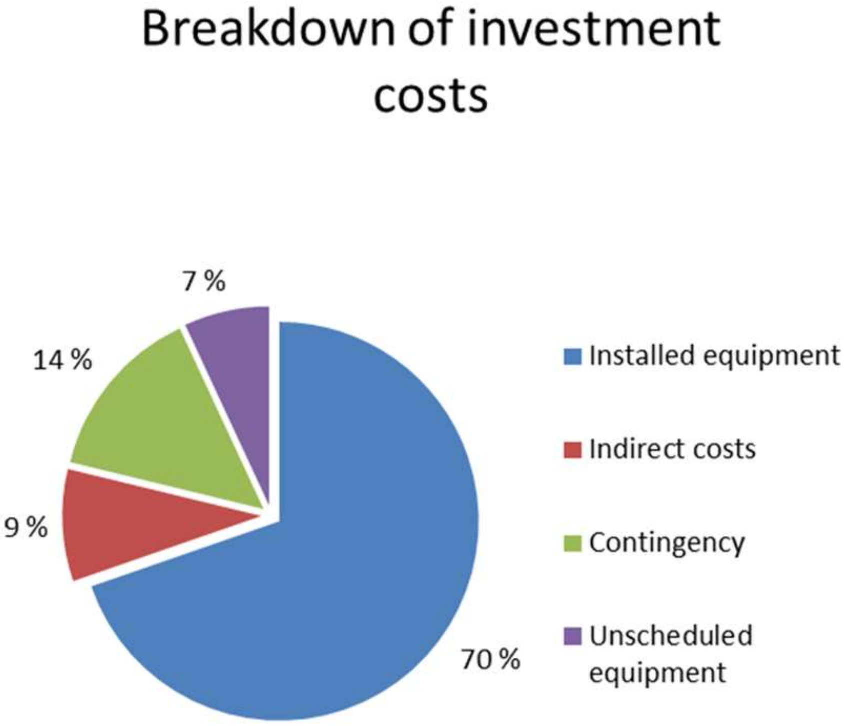
How much does it cost ?

Base Case plant

- Biomass input 1000 dry MTPD(~200 MWth)
- Bio-BTX output 64 kton/a
  (192 MTPD = 16 % mass yield)

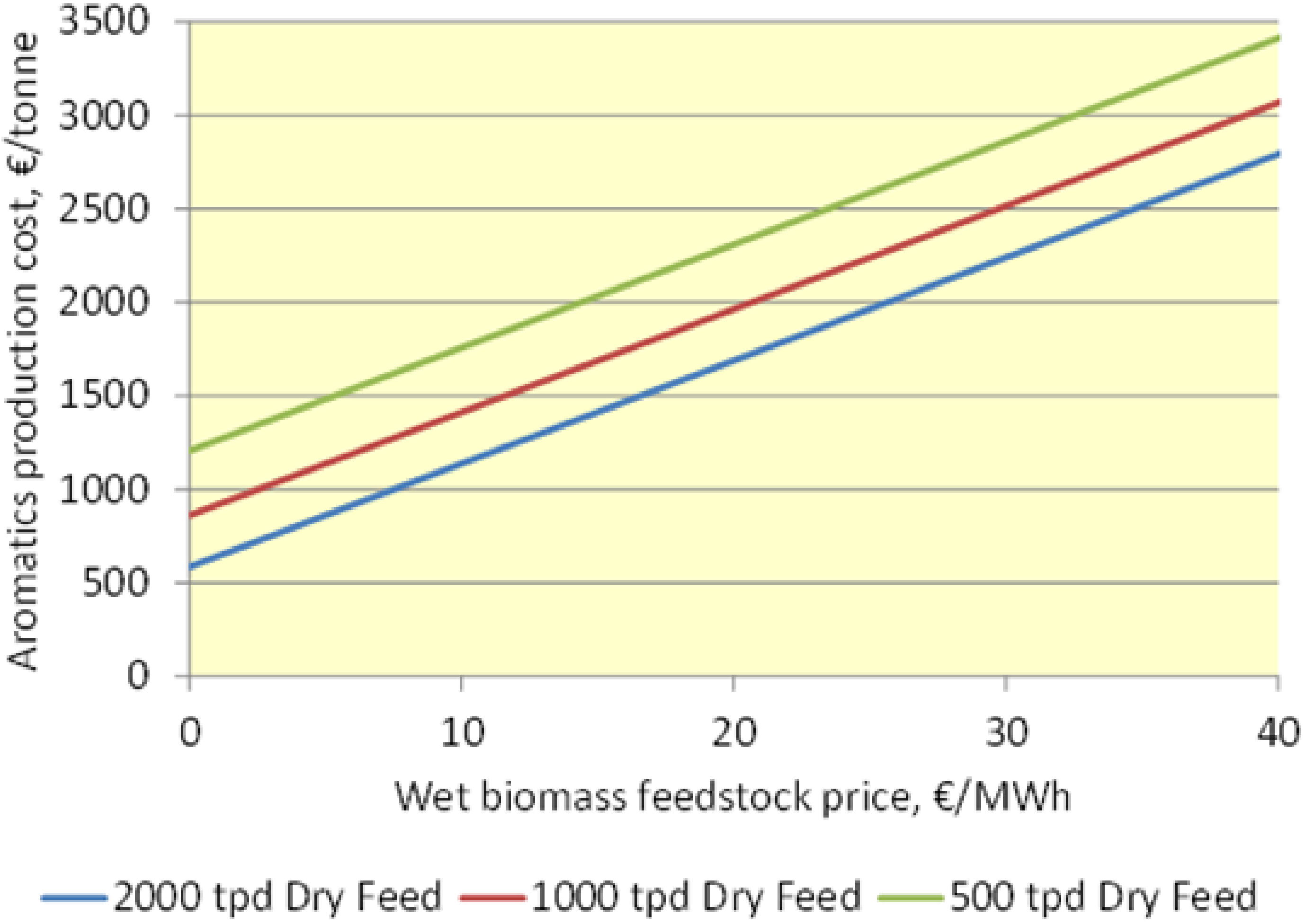
Cost estimates

- Syngas plant = 231 M€
- OT FT-aromatics island = 37 M€
- TOC = 268 M€



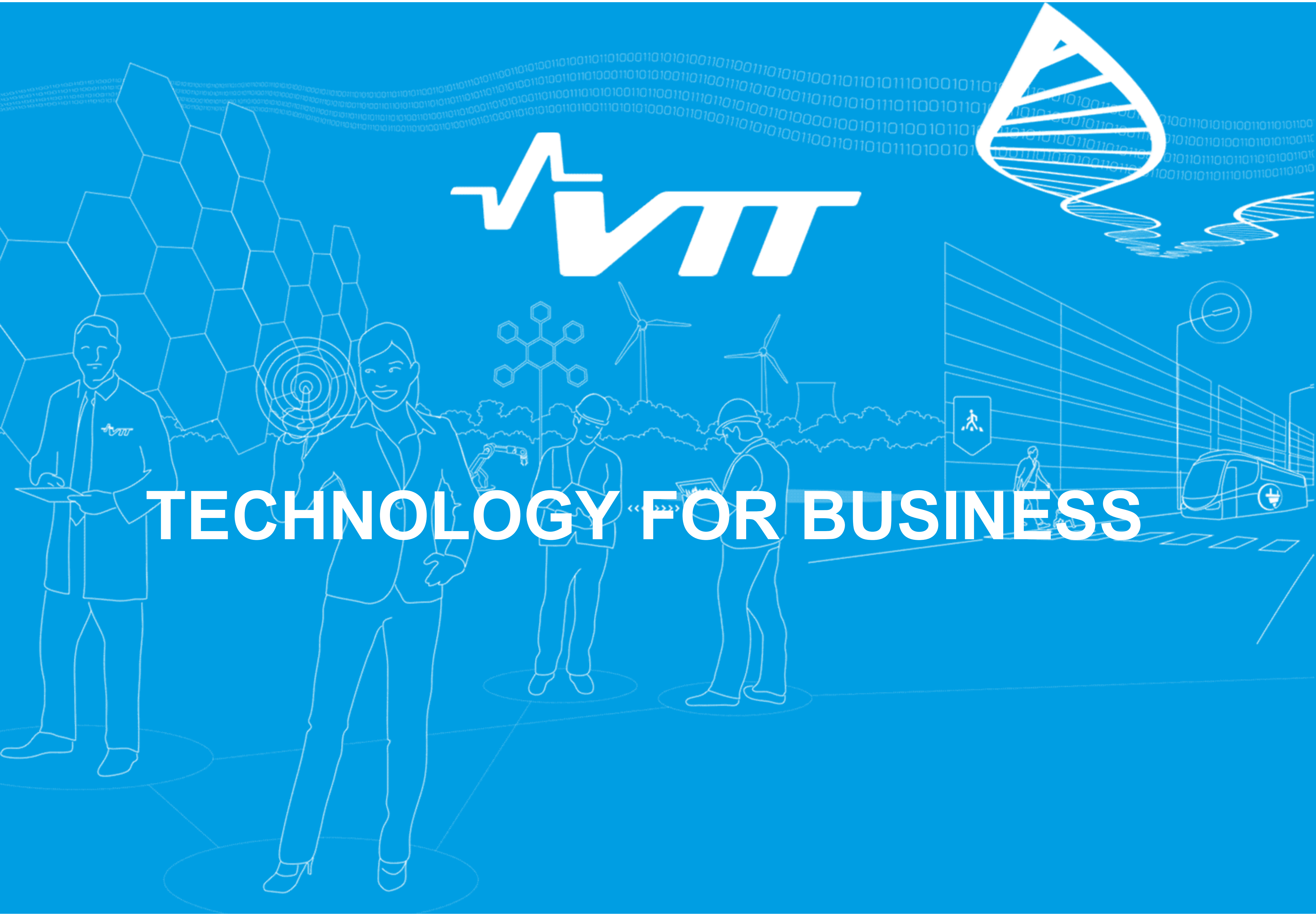
More on cost calculation methodology in a recent VTT publication which can be downloaded at http://bit.ly/192VI3G

Production cost of aromatics vs. biomass price and plant capacity



Conclusions

- We have shown that pure BTX components can be synthesized from biomass derived gas and isolated in high purity. The first estimate of the production cost of bioaromatics is about 1.4 €/kg.
- Bio-BTX can be used as a starting material for demanding end-products such as bio-paracetamol.
- Despite its selectivity the process is a multi-product process
- The next step is to scale-up the process at VTT’s new Bioruukki-piloting facility to demonstrate the whole chain of bio-aromatics production “from stump to the final product”.



TECHNOLOGY FOR BUSINESS