Upgrading of Catalytic Pyrolysis Oil

Steven Gust

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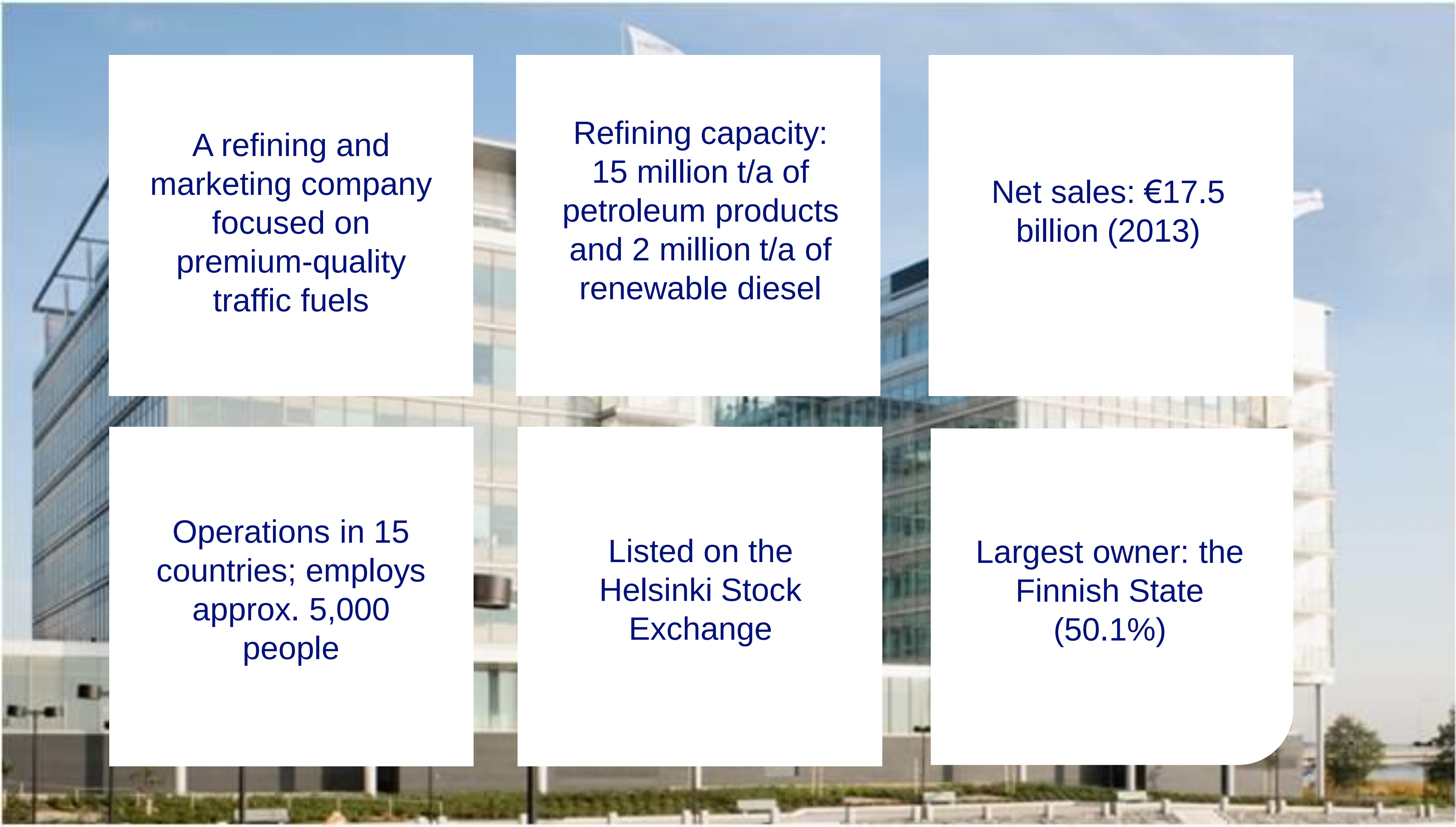
NESTE

Neste in brief



A refining and marketing company focused on premium-quality traffic fuels

Refining capacity: 15 million t/a of petroleum products and 2 million t/a of renewable diesel

Net sales: €17.5 billion (2013)

Operations in 15 countries; employs approx. 5,000 people

Listed on the Helsinki Stock Exchange

Largest owner: the Finnish State (50.1%)

Porvoo Refinery

Vision: To be the preferred partner for cleaner traffic fuel solutions.

Neste presence globally

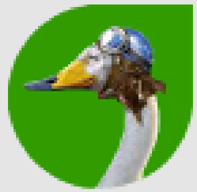
Production:

- Porvoo
- Naantali
- Rotterdam
- Singapore
- Nynäshamn
- Bahrain (joint venture, Neste's share 45%)

Sales and marketing:

- Espoo
- Stockholm
- Tallinn
- Riga
- Vilnius
- St. Petersburg
- Geneva
- Beringen
- Houston
- Toronto
- Dubai
- Singapore

Development of Cleaner Products



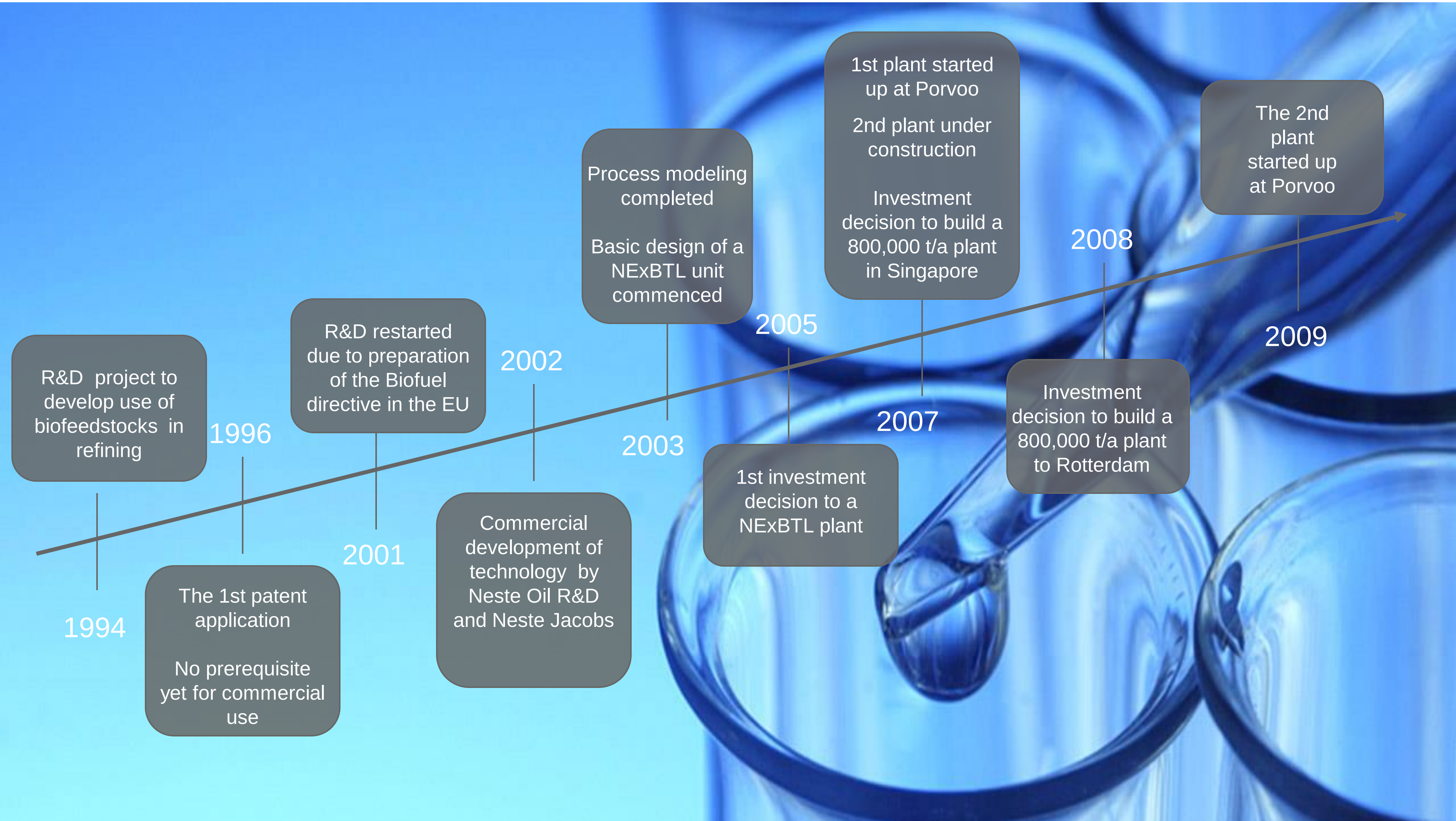
PRO DiESEL

- **80-90**
  - Lead-free city-gasolines
  - Less sulfur -free fuels
  - VHVI base oils
- **2007**
  - Renewable NExBTL diesel
- **2008**
  - Neste Green diesel: 10% renewable NExBTL diesel
- **2010**
  - Neste Green 100: 100% renewable NExBTL diesel
- **2011**
  - Renewable NExBTL aviation fuel
- **2012**
  - Neste Pro Diesel: 15% renewable diesel
  - WWFC specification – the best diesel recommended by the world's car manufacturers
  - NExBTL Renewable naphtha

World’s largest producer of renewable diesel

- Premium-quality NEXBTL provides high performance with a lower carbon footprint.
- Use sustainable raw materials
- Customers include corporate customers in Europe and North America.
- Increasing production capacity to 2.6 million tons by the end of 2016.

NEXBTL Commercialization Pathway



Expanding the feedstock portfolio

Waste animal fat

Waste fish fat

Palm oil fatty acid distillate (PFAD) and stearin

Techical corn oil

Tall oil pitch

Palm oil

Camelina oil

Jatropha oil

Soybean oil

Rapeseed oil

Neste Oil uses also bioethanol obtained from global markets as biocomponent in 95 E10 and 98 E5 gasolines

NEXBTL products

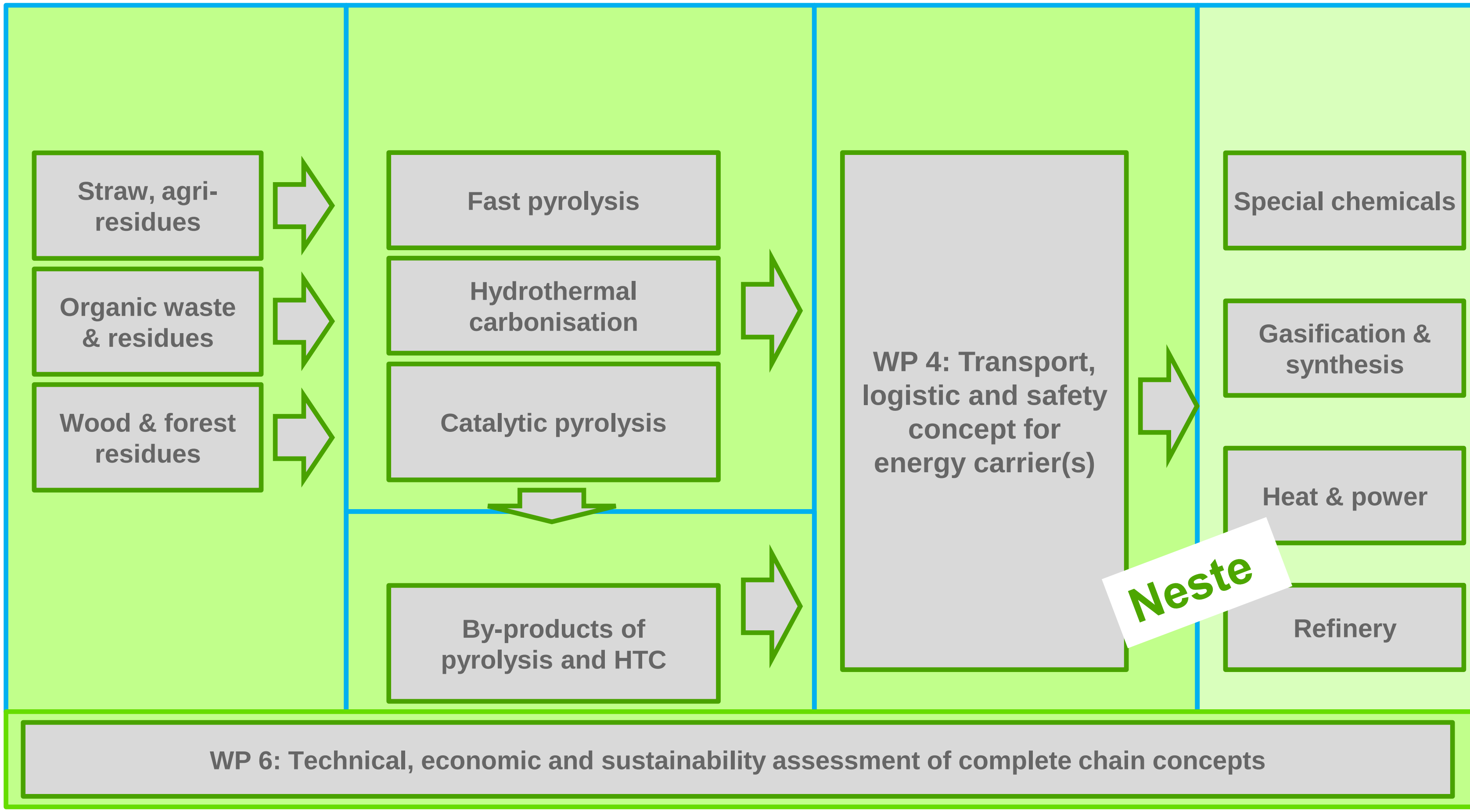
NEXBTL

- NEXBTL renewable **diesel**
- NEXBTL renewable **aviation fuel**
- NEXBTL renewable **naphtha and propane**
- NEXBTL renewable **isoalkane**

BioBoost

This project has received funding from the European Union's Seventh Programme for research, technological development and demonstration under grant agreement No 282873

Neste's Role in BioBoost



Neste Tasks in BioBoost

5.3.1 Evaluation of catalytic pyrolysis oil and selection of reaction

5.3.2 Reactor tests for hydrotreating or catalytic cracking of catalytic pyrolysis oil

5.3.3 Evaluation of different energy carriers, especially catalytic pyrolysis oil, as a feedstock of NESTE Oil refineries

Our tools:

PARR autoclave stirred batch reactor (90 ml)

- 3 g catalyst in a wire mesh basket
- 50 g feed / test

Continuous flow tubular reactor (tube volume 50 ml)

- 24 g catalyst diluted with inert SiC 1:1
- 800 g feed / ~ 6 days

+ lots of analyses

Typical Results

		Feed	Ident2	Ident6	Ident8
Run time	h		25.8	94.7	118.1
Average T	C		298	299	299
Maximum T	C		352	353	353
Pressure	bar		148	148	140
WHSV	h-1		0.3	0.3	0.3
Hydrogen	l/h		12.4	13.7	13.7
Oil sample, wet					
MCR	wt-%	16.8	0.03	0.24	0.15
Density at 15 C	kg/m3	1.18	871	889	889
Viscosity at 20 C	mm2/s		2.4	2.9	2.7
Water	wt-%	5.0	0.01	0.043	0.085
Oil sample, dry					
H	wt-%	7.1	12.4	11.5	11.7
C	wt-%	76.1	86.2	85.4	86.7
N	wt-%	0.065	0.001	0.015	0.015
O, calculated	wt-%	16.8	1.4	3.0	1.5
H/C	mol/mol	1.11	1.71	1.60	1.61
O/C	mol/mol	0.17	0.01	0.03	0.01
Degree of HDO	%		94	86	93
Degree of HDN	%		99	86	86

Experimental Results Summary

- oil product yield was approximately 73 wt%
- hydrogen consumption (based on dry CP oil feed) was 6 wt%
- non-condensable gases (13 wt%) primarily paraffinic hydrocarbons
- CP oil feed requires a stabilization step; catalyst coking could not be prevented
- under the operation conditions used, we were not able to remove all oxygen

Choice of Concept

CP OIL Upgrading Criteria

1. chemical and physical composition
2. miscibility with hydrocarbons
3. tendency to coke
4. EU legilsation
5. isolation of products
6. availability of oil refinery units

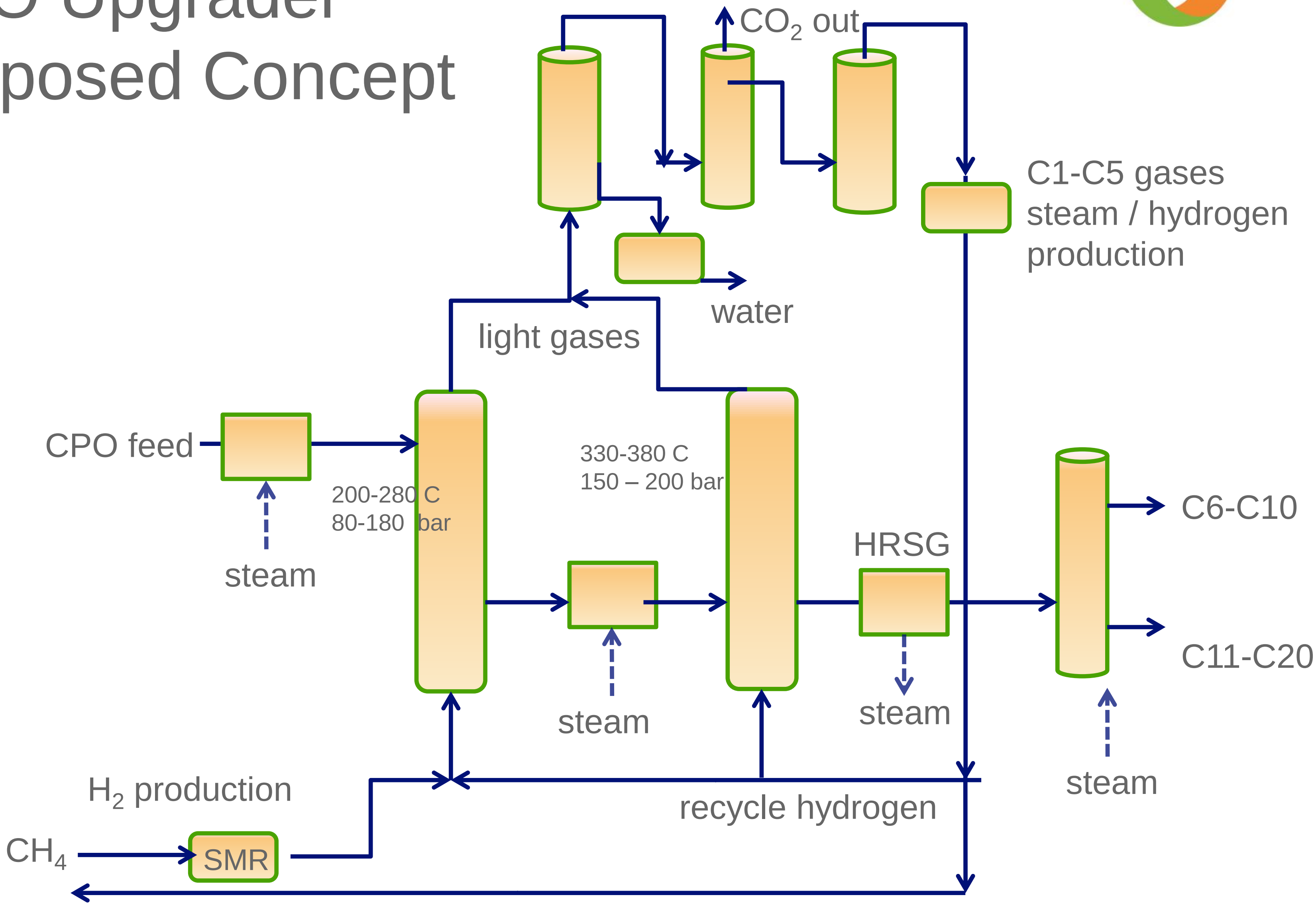
CP Oil Upgrading Proposed Concept

two stage hydrotreating:
1st stage stabilization, 2nd stage hydrodeoxygenation

separate units but integrated into refinery infrastructure utilizing refinery hydrogen, power and steam and waste water

3rd stage possibly required

CPO Upgrader
Proposed Concept



Lessons Learned

1. CP oil is aromatic so processes with hydrogen added are preferred from a yield standpoint
2. much simpler / easier to upgrade CP oil than TP oil based on our results compared to TP upgrading in literature
3. stabilization is required to prevent coking on catalyst; optimum conditions not yet found
4. hydrogen consumption is moderate and could be produced (at least partially) from off gases
5. catalysts did show coking after 3-4 days so conditions (T, H_2 pressure, catalyst etc.) must be further optimized
6. in order to design a commercial process further upgrading studies are required

Neste Conclusions to Date

1. Reactive components are present in CP oil which will require stabilization step
2. Once adequate conditions were found, it was quite easy to upgrade the CP oil.
3. Coking of catalysts occurred even with stabilization indictating that optimum conditions have not yet been found
4. Conclusions are preliminary as no long term (> 3 months) catalyst testing could be performed within the BioBoost project
5. Fuel quality issues remain to be answered
6. It should be possible to resolve these issues provided sufficient CP oil is available for testing