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Development Status of Biomass Fast Pyrolysis 2016

December 15 2016, Espoo

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Technical Research Centre of Finland Ltd





Summary

- This is a concise report on the development status of biomass fast pyrolysis in 2016. Three industrial scale plants have been built, those from Valmet, BTG, and Ensyn. The product, pyrolysis bio-oil, is used to replace heating fuel oils or natural gas to fuel boilers (Finland, Netherlands, USA).
- Only very limited data is available on amounts of produced bio-oil in open literature.
- Development efforts are on-going to upgrade the primary oxygen containing acidic bio-oil also to transportation fuels. Much of the work is still in laboratory scale. However, a notable exception is a more recent development, where bio-oil is co-refined at existing mineral oil refinery unit. Co-refining of both BTG and Ensyn oils have been carried out by Petrobras in their pilot unit.
- Catalytic fast pyrolysis of biomass has been proven in pilot-scale. Scale-up to industrial scale will probably still take a few years.
- Economic competitiveness of bio-oil production is obviously a function of mineral oil cost. Without subsidies, current mineral oil prices don't support using the current bio-oil quality for heating. However, co-refining in a FCC-unit for bio-components to existing fuels appears to be a real alternative, provided remaining technical issues will be solved.



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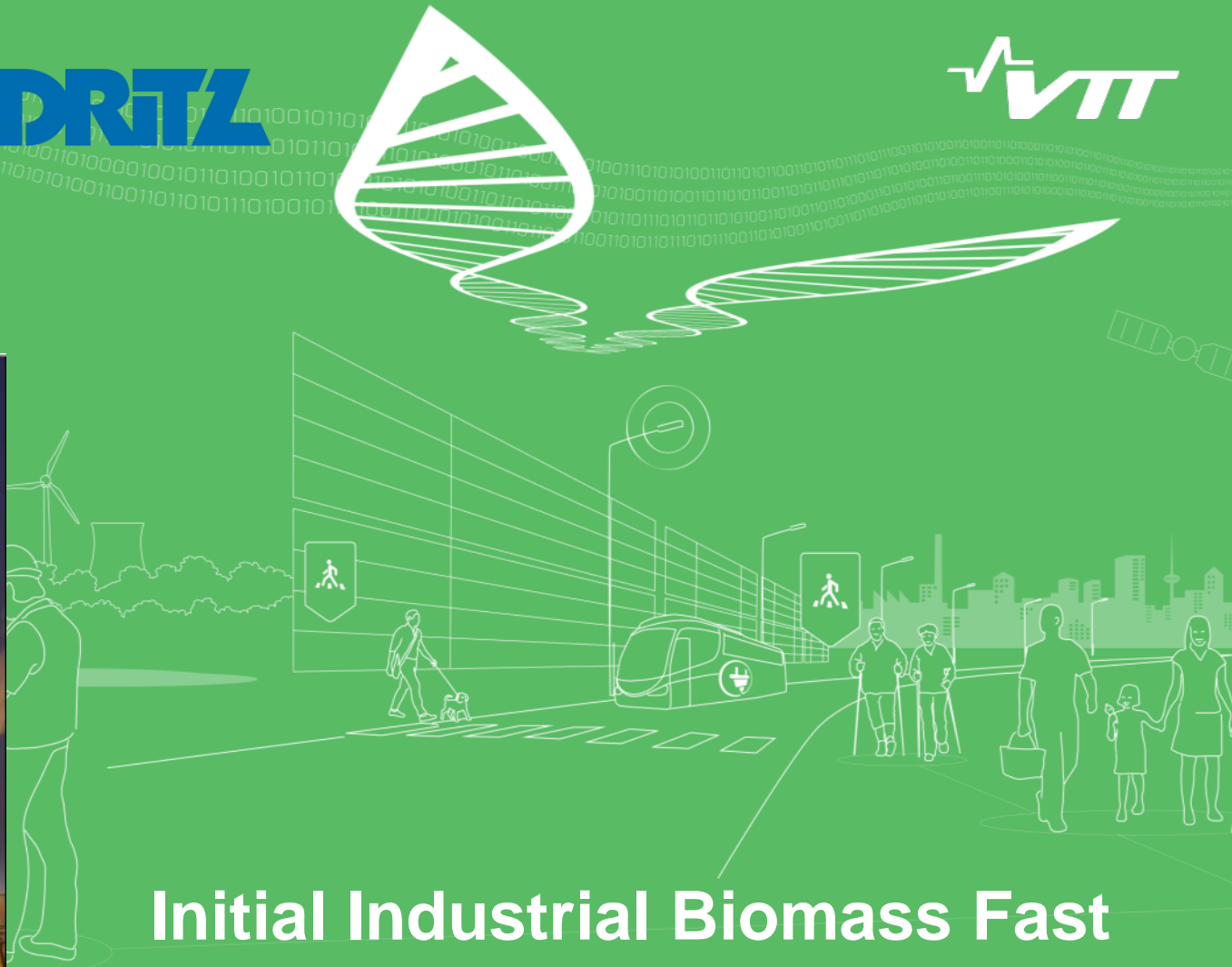
- Initial Industrial Biomass Fast Pyrolysis Developments
- Fast Pyrolysis of Forest Residues - Cost and Performance Analysis
- Co-Refining of Fast Pyrolysis Bio-Oils with Mineral Oils in FCC Units
- State of the Art of Bio-oil Hydroprocessing
- Catalytic Fast Pyrolysis
- Future developments
- Markets
- VTT Bio-Oil Characterization Built to Serve industrial Efforts and Standardization

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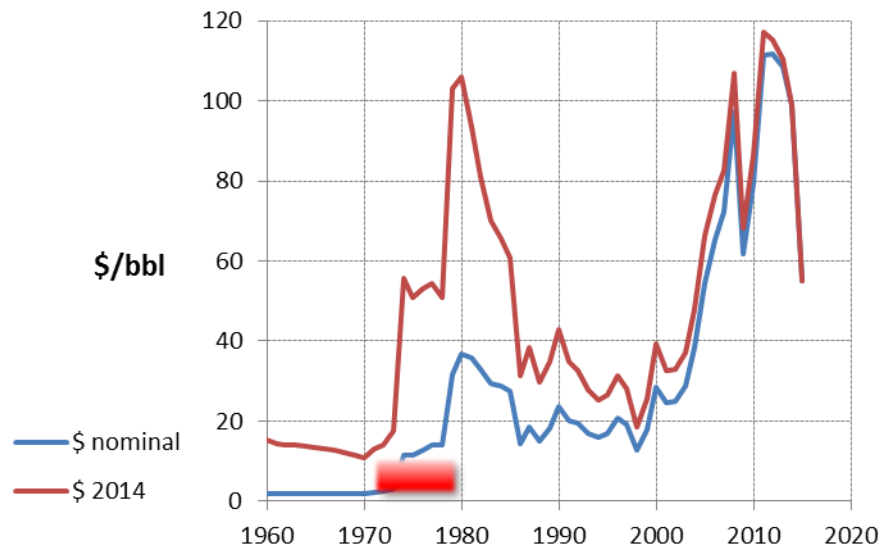
VTT



Initial Industrial Biomass Fast Pyrolysis Developments

Garrett & Occidental – A Concept Inspired by the Fluid Catalytic Cracker (FCC)

- Pioneering work with fast pyrolysis by Garrett Research, later at Occidental Petroleum using urban waste in the USA during the 70's. Several patents and applications are available.
- “During the last three years the Garrett Research and Development Company has developed an integrated resource recovery ..., and the organic components are converted to good quality fluid fuels.” *



United States Patent 4,153,514

Garrett et al.

May 8, 1979

[54] **PYROLYSIS PROCESS FOR SOLID WASTES**

[75] Inventors: **Donald E. Garrett**, Claremont;
George M. Mallan, Pomona, both of Calif.

[73] Assignee: **Occidental Petroleum Corporation**,
Los Angeles, Calif.

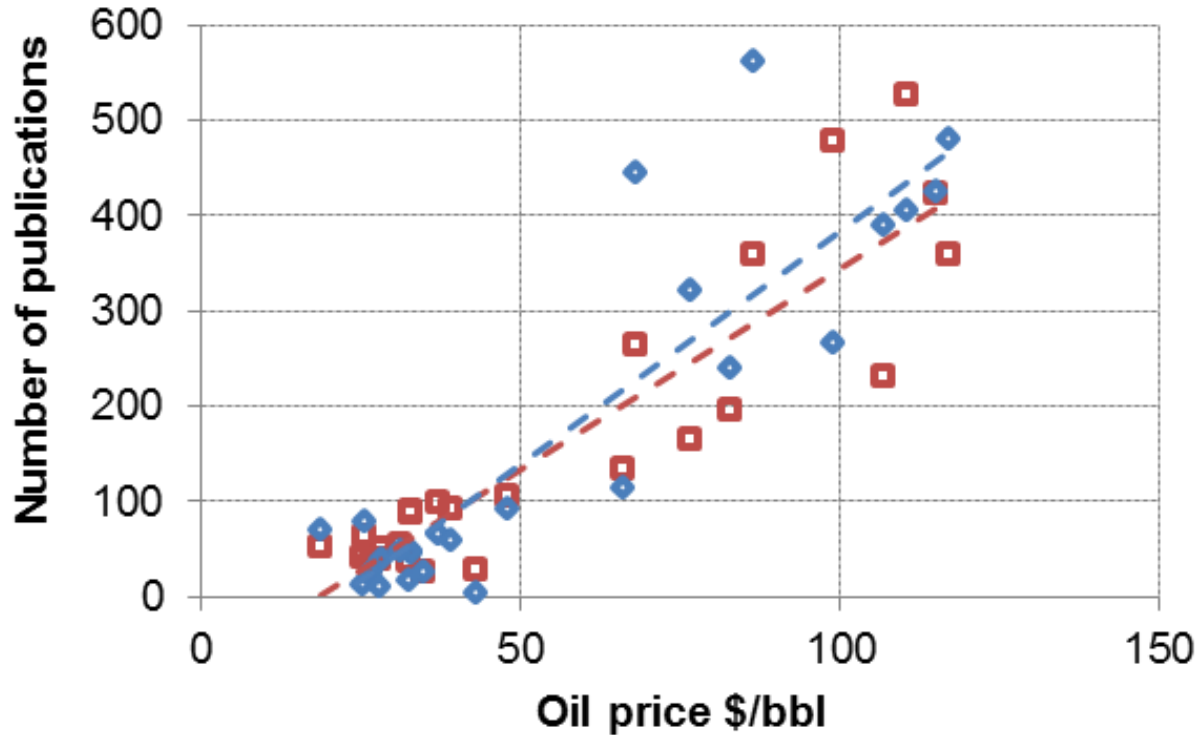
[21] Appl. No.: **687,150**

[22] Filed: **May 17, 1976**

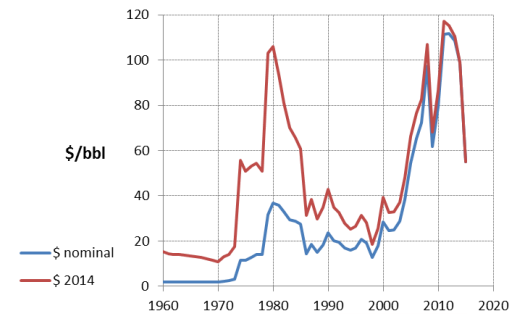
* C. S. FINNEY & D. E. GARRETT, *The Flash Pyrolysis of Solid Wastes*. *Energy Sources*, Volume 1, Issue 3, 1974, pages 295-314



Oil Price vs Papers and Patent Applications "Fast pyrolysis"



A two year delay assumed from oil price to publication, data after 1989->. Data from Scopus and bp-statistical-review-of-world-energy-2015-workbook.xlsx



Fast Pyrolysis for Bio-Fuel Oil - Scale-Up



UNION
FENOSA, SPAIN



FORTUM, PORVOO, FINLAND



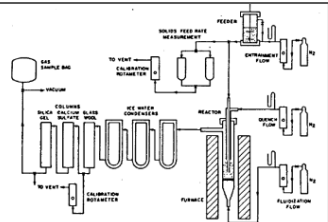
FORTUM DEMONSTRATION - JOENSUU, FINLAND



ENEL, BASTARDO, ITALY



VALMET, TAMPERE, FINLAND



UNIVERSITY OF
WATERLOO, CANADA

1980	1985	1990	1995	2000	2005	2010	2015
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EARLY FAST PYROLYSIS BENCH-SCALE

- Canada, USA
- IEA bioenergy assessments

FIRST EUROPEAN PILOTS 1994-2000

- Two Canadian, one Finnish technology
- Continuous operation verified
- Operated by European utilities

SCALE-UP 2004 - 2015

- ENSYN in Canada
- BTG in Malaysia
- VALMET 2008-
- FORTUM demonstration 2014
- BTG demonstration 2015

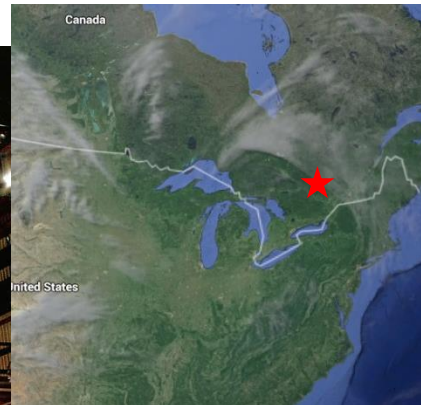
Ensyn (Can) – Plants in Canada & USA



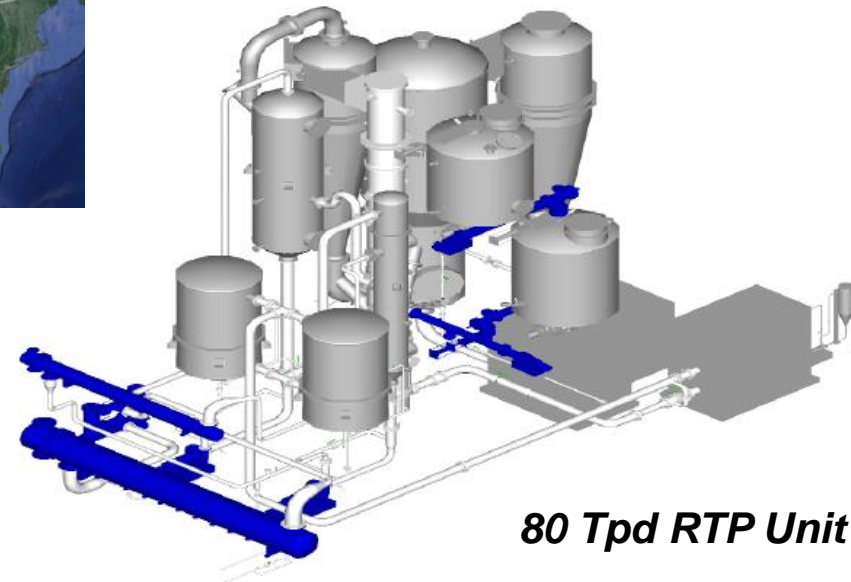
- Commercial production of smoke flavour compounds in smaller units
- Ensyn's largest RTP™ at The Renfrew (9 MW of oil) plant has been in operation since 2006, focused primarily on production of liquids and heating fuels for the specialty chemicals industry.
- The plant was upgraded 2014 to the current capacity.



8.12.2016



<http://www.ensyn.com/>



80 Tpd RTP Unit



Ensyn - Production

- Ensyn has announced two delivery contracts for its Renewable Fuel Oil (RFO) <http://www.ensyn.com/ontario.html>
- In 2014 Ensyn Fuels signed a five year contract with Memorial Hospital, North Conway, New Hampshire. Deliveries under this contract have taken place since August 2014 and are ongoing.
- In 2015 Ensyn Fuels signed a five year contract with Youngstown Thermal LLC (Youngstown, Ohio) for the supply of RFO for their district heating operations. Deliveries began in May of 2016.
- Based on this information and EPA's Renewable Fuel Standard Data it may be deducted that Ensyn has delivered total of 1 994 tons of RFO to these users since August 2014.



Ensyn – Projects 1

- The most developed of the numerous Ensyn projects is the Cote Nord Project is a 10.5 million gallons/year (approximately 40 million litres/year) biocrude production facility located in Port-Cartier, Quebec. The Cote Nord Project will convert approximately 65,000 dry metric tons per year of slash and other forest residues from local sources to biocrude.
<http://www.ensyn.com/quebec.html>
- However, based on <http://www.tvanouvelles.ca/2016/07/04/le-groupe-remabec-innove-a-parent> it appears that the contract in place concerns first constructing a facility with a design capacity of 10 800 t/a (about 7.7 MW) of bio-oil.
- The project has larger goals, once the first reactor is successfully in production.

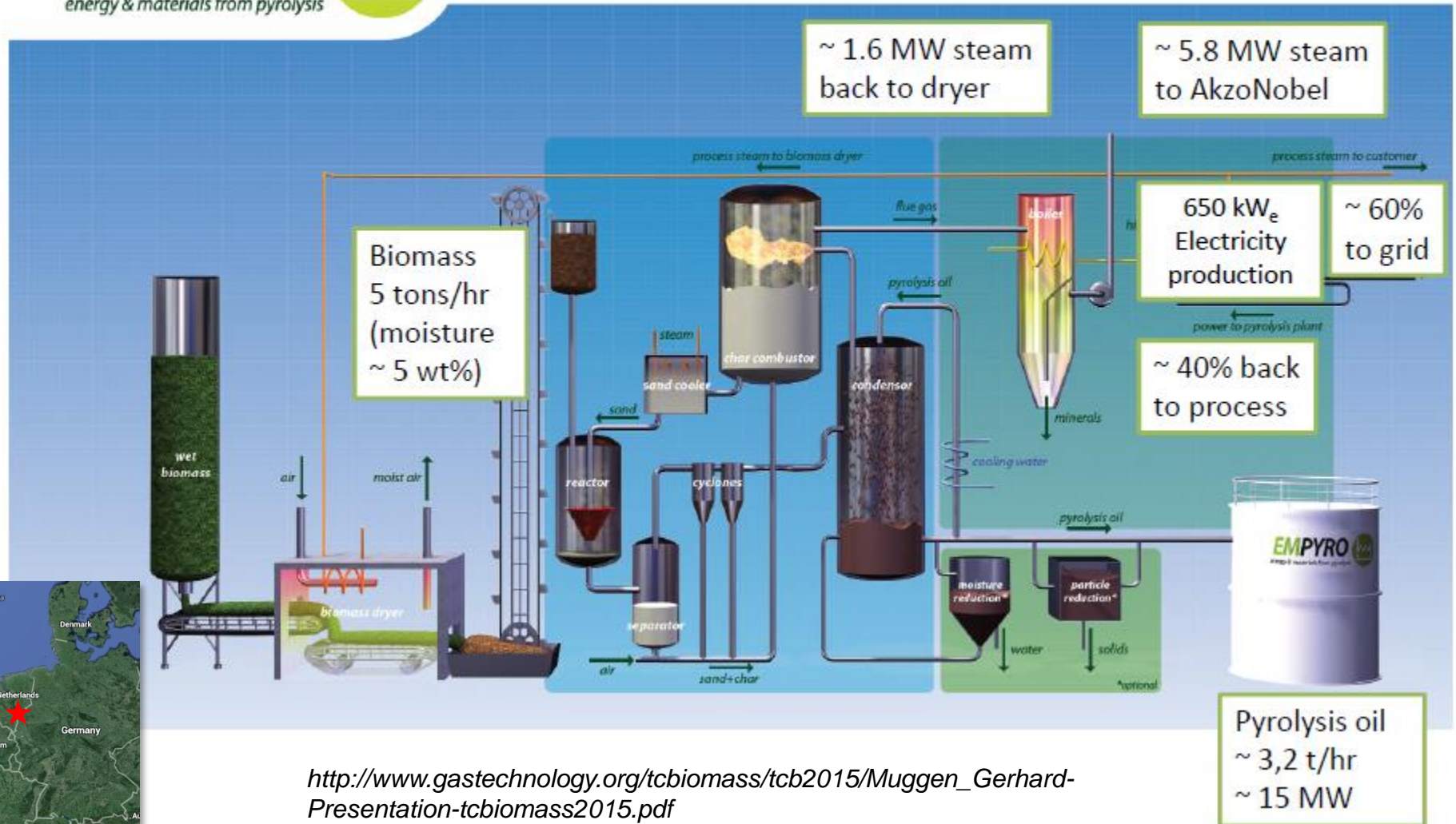


Ensyn – Projects 2

- Ensyn has a JV with Fibria.
- The Aracruz Project is a 22 million gallon/year biocrude production facility being developed by Ensyn and Fibria Celulose S.A. in a 50/50 partnership. The project is co-located at Fibria's 2.3 million tonne/year pulp facility at Aracruz, Espirito Santo, north of Rio de Janeiro.
- Feedstock for the project is eucalyptus residues from the Aracruz mill supplemented by material from local, managed plantations. Biocrude will be shipped to refinery and heating/cooling markets in the U.S.
- This project has been in development stage since 2012.

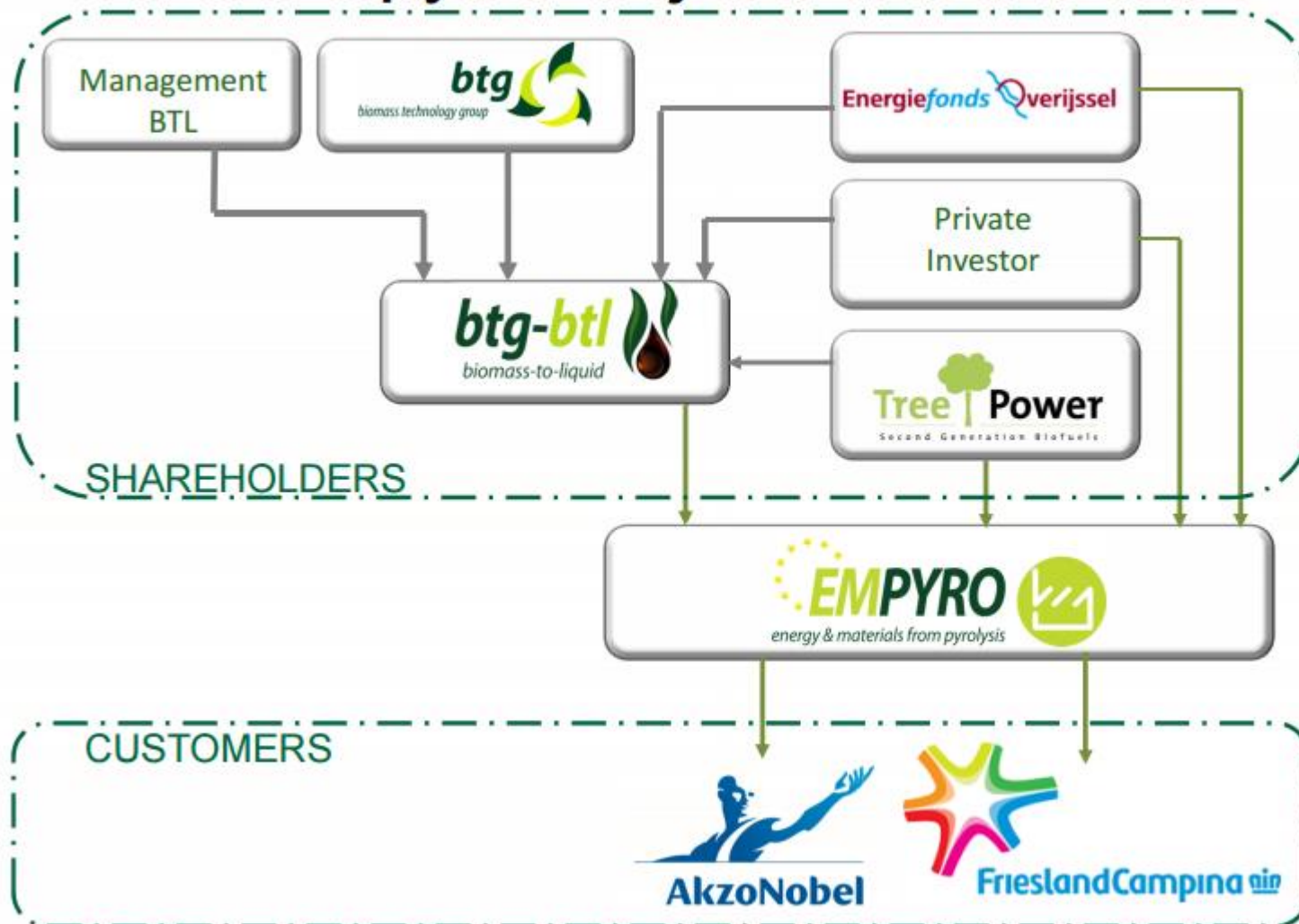


Key Process Figures



http://www.gastechnology.org/tcbiomass/tcb2015/Muggen_Gerhard-Presentation-tcbiomass2015.pdf

Empyro Project Stakeholders



Pyrolysis oil, the sustainable alternative



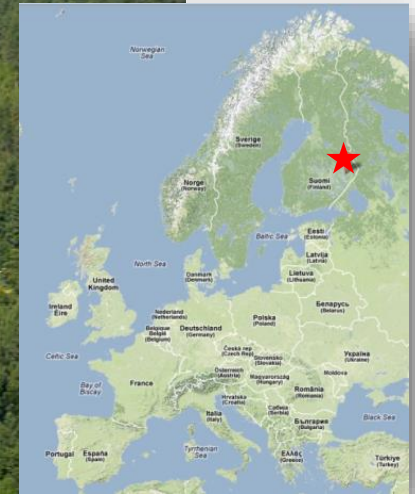
Empyro – BTG/BTL

- Empyro BV (stakeholder and owners in the previous page) has constructed a demonstration plant at a Akzo Nobel chemical plant site in the Netherlands. The plant has been in operation since 2015.
- In May 2016*: 3 - 4 million litres produced, which corresponds to about 3 600 - 4 800 t. At full design capacity, this would correspond to about 1 100 to 1 500 h.

** A presentation in the BOBIC/IEA workshop 2016-06-14 "Commercial Scale Fast Pyrolysis Oil Production and Utilisation" by Bert van De Beld, BTG.*

Integrated Pyrolysis at the Fortum Combined-Heat-and-Power Plant in Joensuu

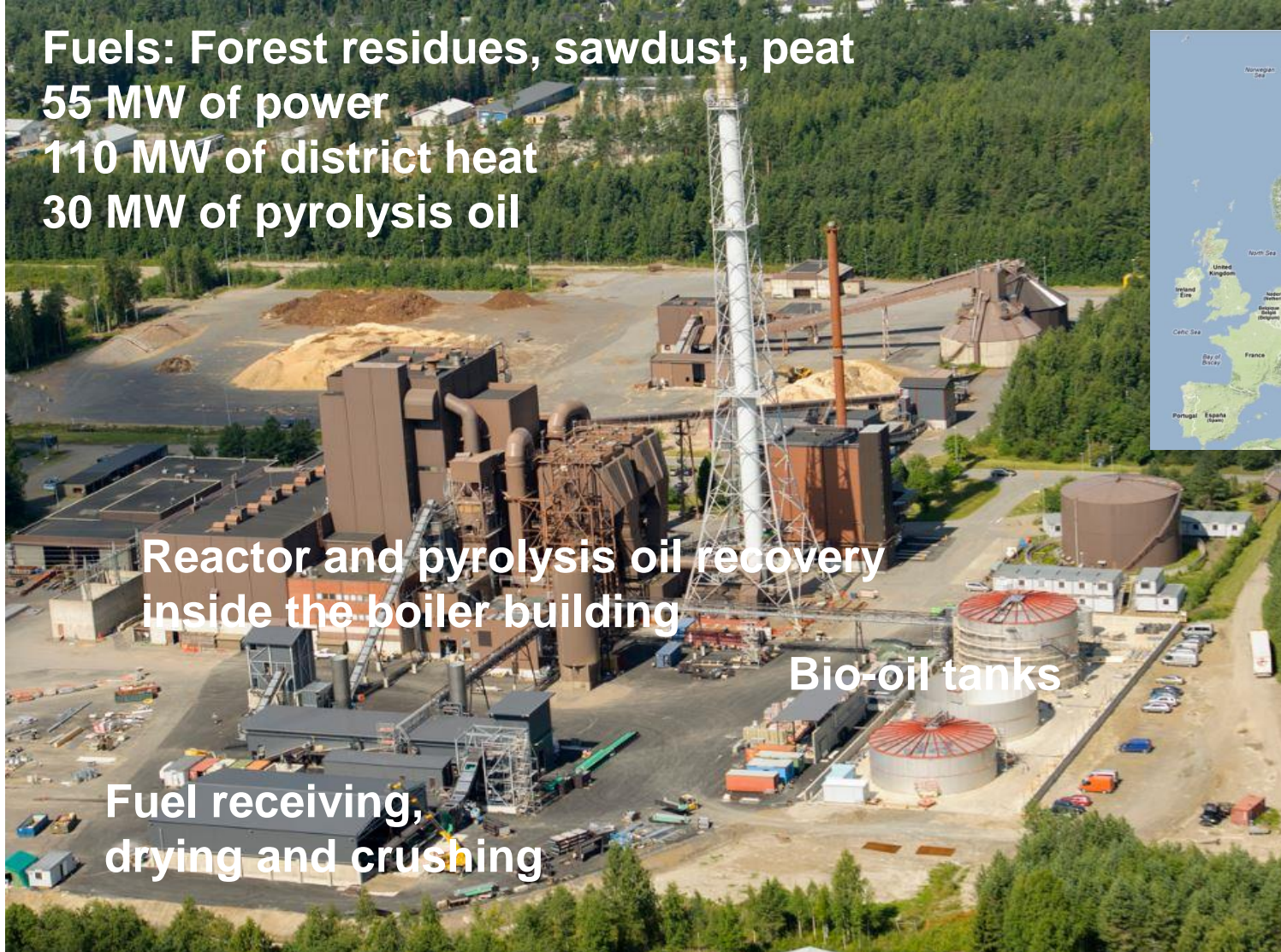
Fuels: Forest residues, sawdust, peat
55 MW of power
110 MW of district heat
30 MW of pyrolysis oil



Reactor and pyrolysis oil recovery
inside the boiler building

Bio-oil tanks

Fuel receiving,
drying and crushing





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Fortum Joensuu

- Built by Valmet under a license from VTT.
- Commissioning was started 2013.
- The plant was handed to the customer June 30, 2015.
- The only production figure available is the "By the end of March 2014, about 600 tons of bio-oil had been produced"*.

* <http://pennwell.sds06.websds.net/2014/cologne/pge/slideshows/T2S2O40-slides.pdf>



Fortum

Joensuu: an Integrated Bio-Oil Demonstration Plant

- Bio-oil capacity 30 MW
- Annual production 50 000 t, 210 GWh
- Start-up 2013
- Feedstock Forest residues, sawdust

Reactor and pyrolysis oil recovery inside the boiler building

Fuel receiving, drying and crushing

VTT contribution

- The integrated concept, ITP
- Operational skills from pilot to demonstration
- Applications in boilers and engines
- Active role in ASTM & EN standardization
- Product quality control

Bio-oil tanks

Technology supplied by



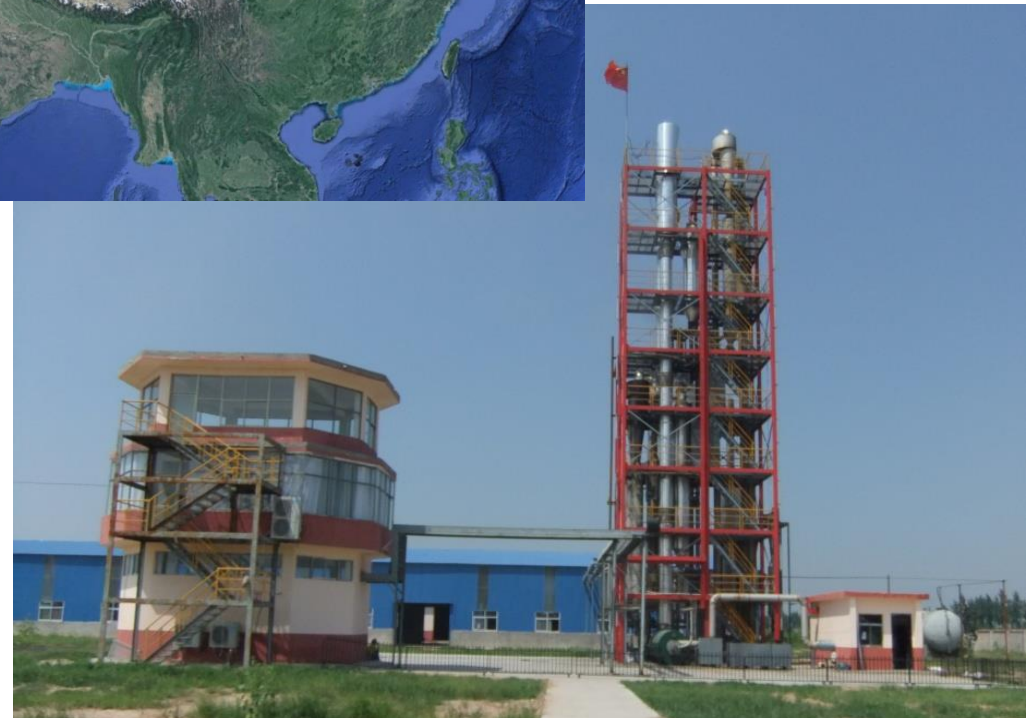


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Demonstration of bio-oil production - Shanghai JiaoTong University & Shanxi Yingjiliang Company, China

- Professor Ronghou Liu from Shanghai JiaoTong University, China coordinated a demonstration project in Shaanxi, China 2011-2013.
- Bio-oil capacity of the plant is 10 000 t/a, and the bio-oil was used for heating of bitumen/asphalt.





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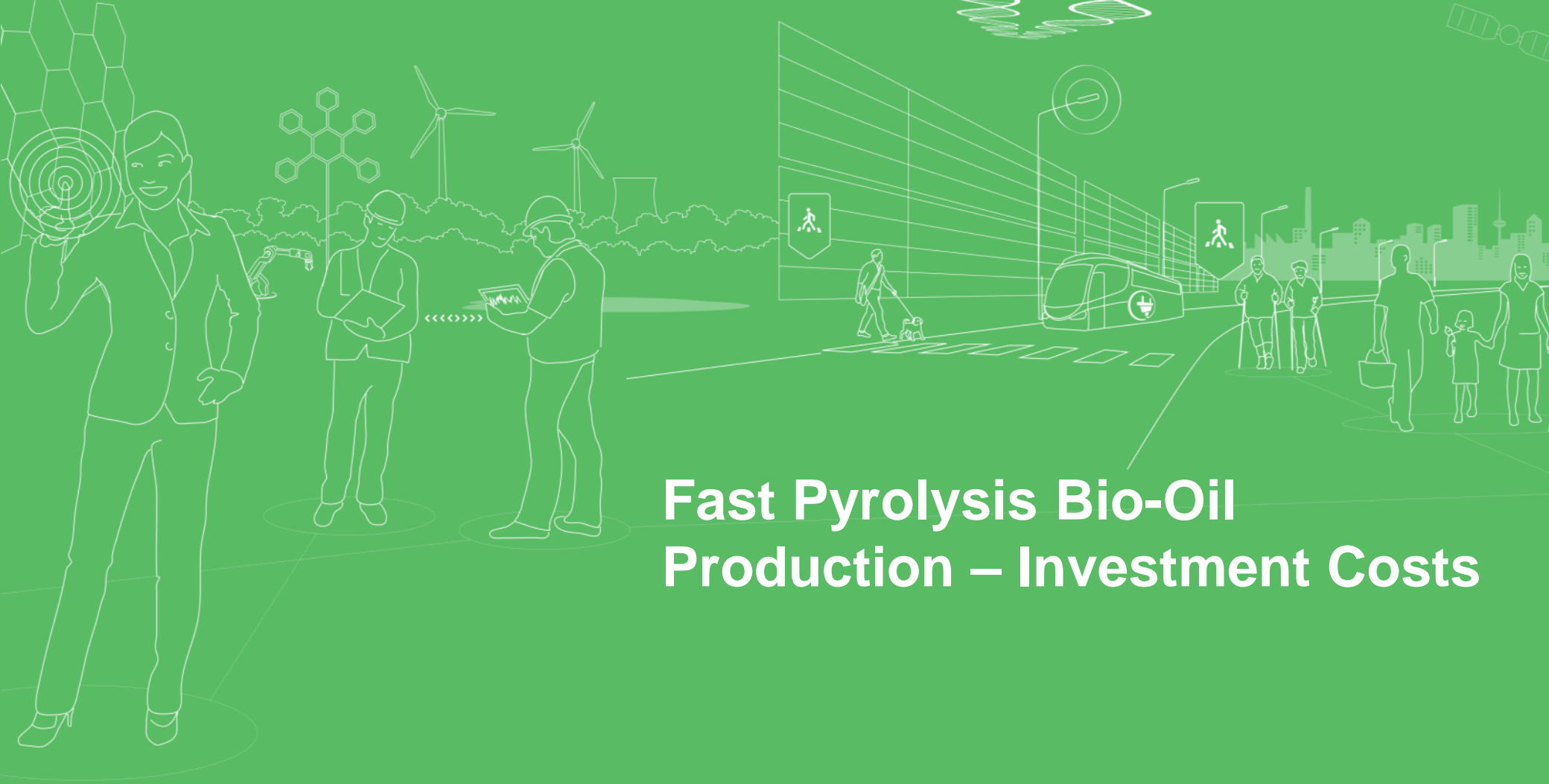
Demonstration of bio-oil production - Shanghai JiaoTong University, Shanxi Yingjiliang Company, China

- No production figures are available
- The current status is believed to be dormant



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Fast Pyrolysis Bio-Oil Production – Investment Costs



CAPEX

- 2012 - Fortum 30 M€* - However, this number includes also non-pyrolysis plant facilities. Design capacity 30 MW_{th} of oil.
- 2014 - Empyro 19 M€**. Design capacity 14 MW_{th} of oil.
- 2011- No investment costs from Ensyn are available. However, based on the information from GFN***, a cost of 50 M€ for a 54 MW_{th} oil plant has been published.
- Thus a specific investment cost between 930 to 1 300 k€/MW_{th} may be calculated.

* <http://www.fortum.com/en/mediaroom/pages/fortum-invests-eur-20-million-to-build-the-worlds-first-industrial-scale-integrated-bio-oil-plant.aspx>

** http://www.empyroproject.eu/uploads/documenten/140208Press_release.pdf

*** <http://www.tekniikkatalous.fi/tekniikka/energia/2011-10-12/Green-Fuel-Nordic-rakentaa-kolme-biojalostamoja-Suomeen-3304805.html>



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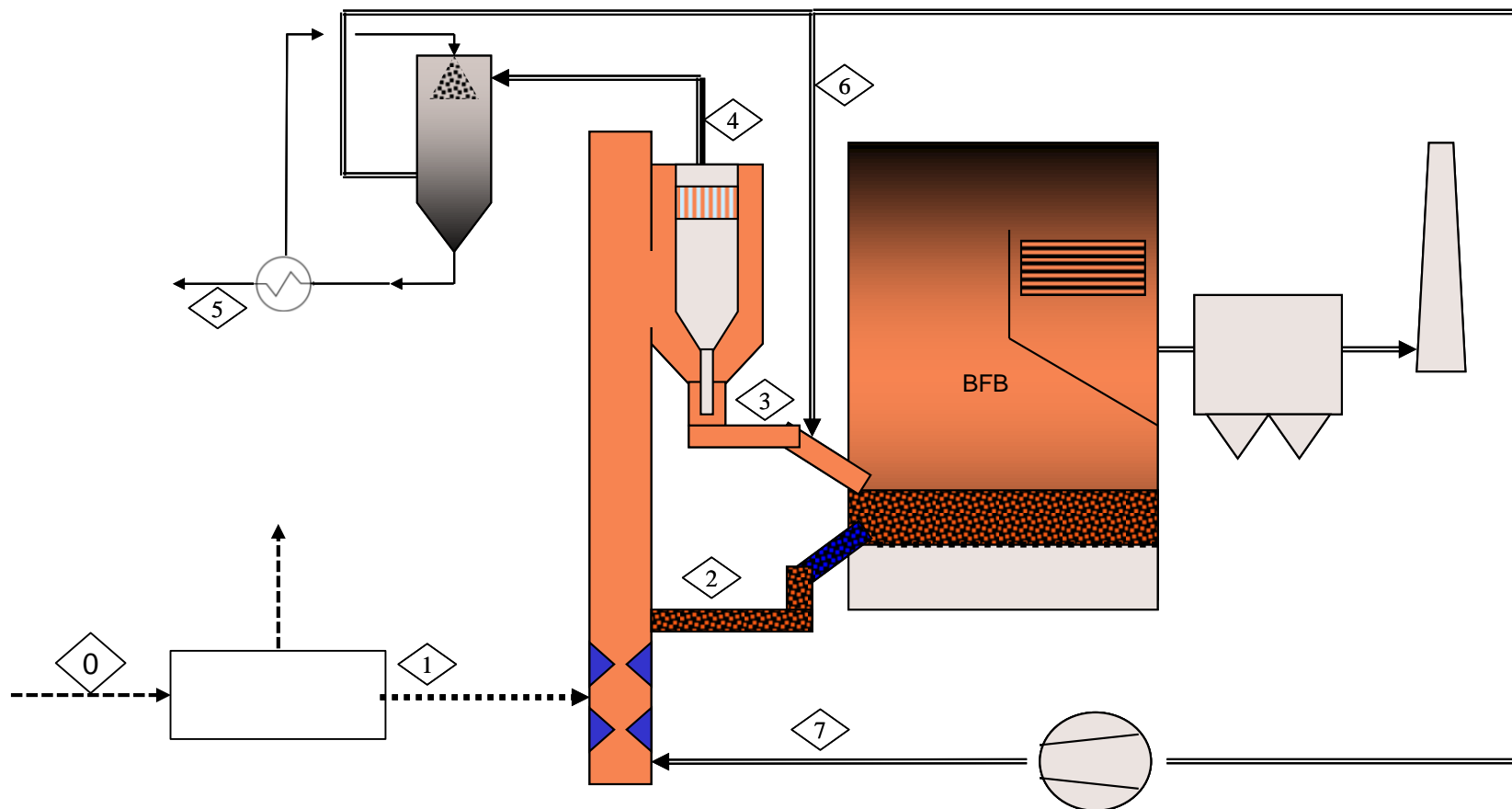


Fast Pyrolysis of Forest Residues - Cost and Performance Analysis



Bases for the assessment

- Performance
 - Feed: Forest residues with an organic yield of 51.2 wt % (dry oil from dry feed)
 - Input: 5.8 kg/s of 50 wt% wet forest residue (48.3 MW)
 - Output: 2.1 kg/s of bio-oil with 29.1 wt% moisture (30 MW)
 - Additionally 6.5 MW of extra heat from the boiler (drying demand has been taken into account), valued as district heat in economic assessment
- Economic assessment
 - Capital costs evaluated with capital recovery factor 0.12 (base case 10 %, 20 a)
 - Feed 20 €/MWh
 - Other operation costs as in chemical processing industries
 - Investment cost 940 k€/MW_{th} of oil (VTT in house data)



Fast Pyrolysis of Forest Residue 8 wt%
VTT
Andritz 17.11.2016

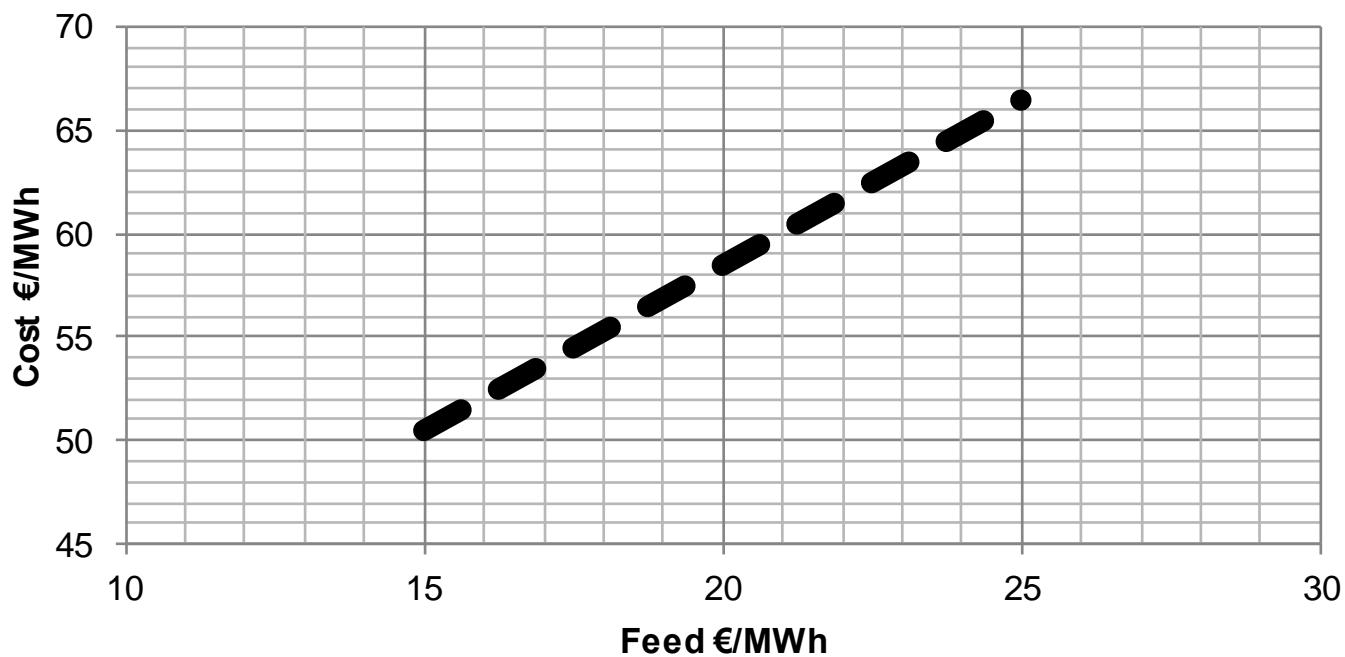


Main process flows

	0	1	2	3	4	5	6	7
	WOOD TO	WOOD TO	SAND TO	CHAR TO	PYROLYSIS	PRODUCT	PURGE GAS	RECYCLE
	DRYER	PYROLYSIS	PYROLYSIS	BOILER	VAPOURS	LIQUID		GAS
Temperature C	15	15	800	504	480	25	35	35
Pressure bar	1.0	1.0	1.0	1.0	1.2	1.0	1.0	1.2
Volume flow m3/s					14.77		0.29	5.82
Total mass flow kg/s	5.77	3.14	34.18	34.89	9.65	2.08	0.35	7.21
Non-condensables					7.19		0.34	6.86
Water	2.89	0.25			0.71	0.61	0.01	0.10
Organics					1.74	1.48	0.01	0.25
Char				0.70				
Dry wood	2.89	2.89						
Sand			34.18	34.18				
Chemical energy MW	48.3	54.7		22.0		30.2	3.7	
Heating value MJ/kg	8.4	17.5		31.3		14.5	10.4	



Bio-Oil Production Cost as a Function of Feed Cost

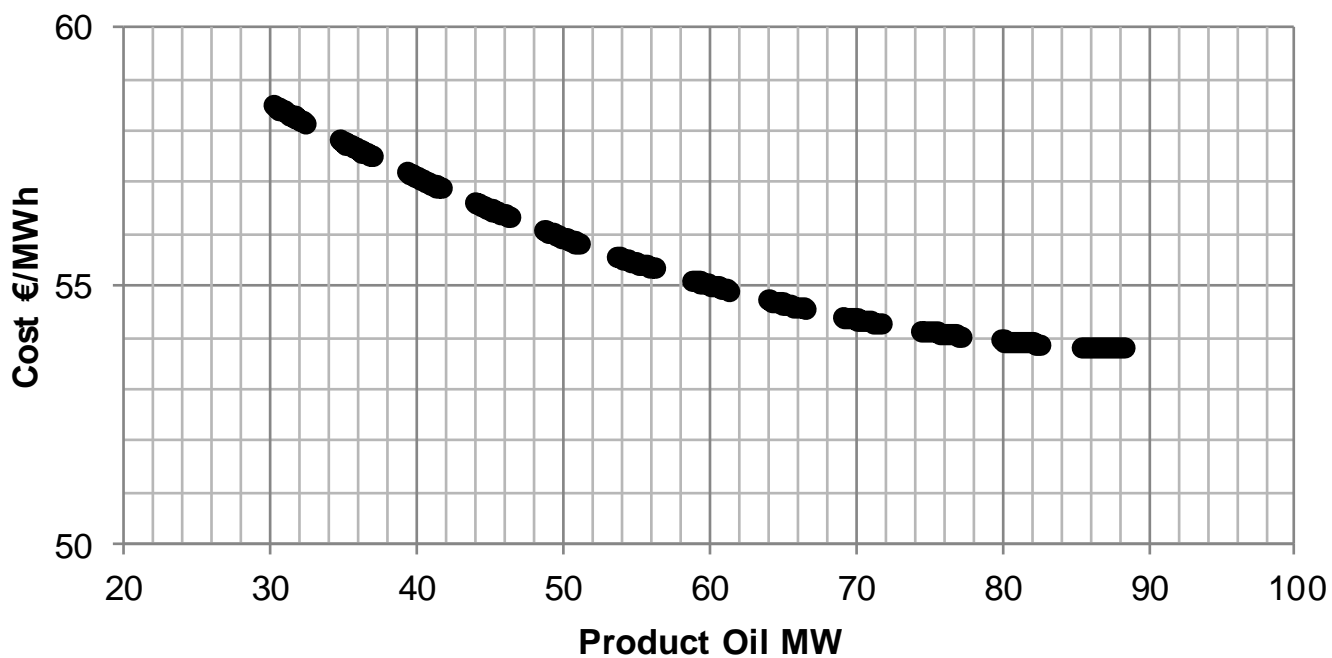




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Bio-Oil Production Cost as a Function of Production Capacity

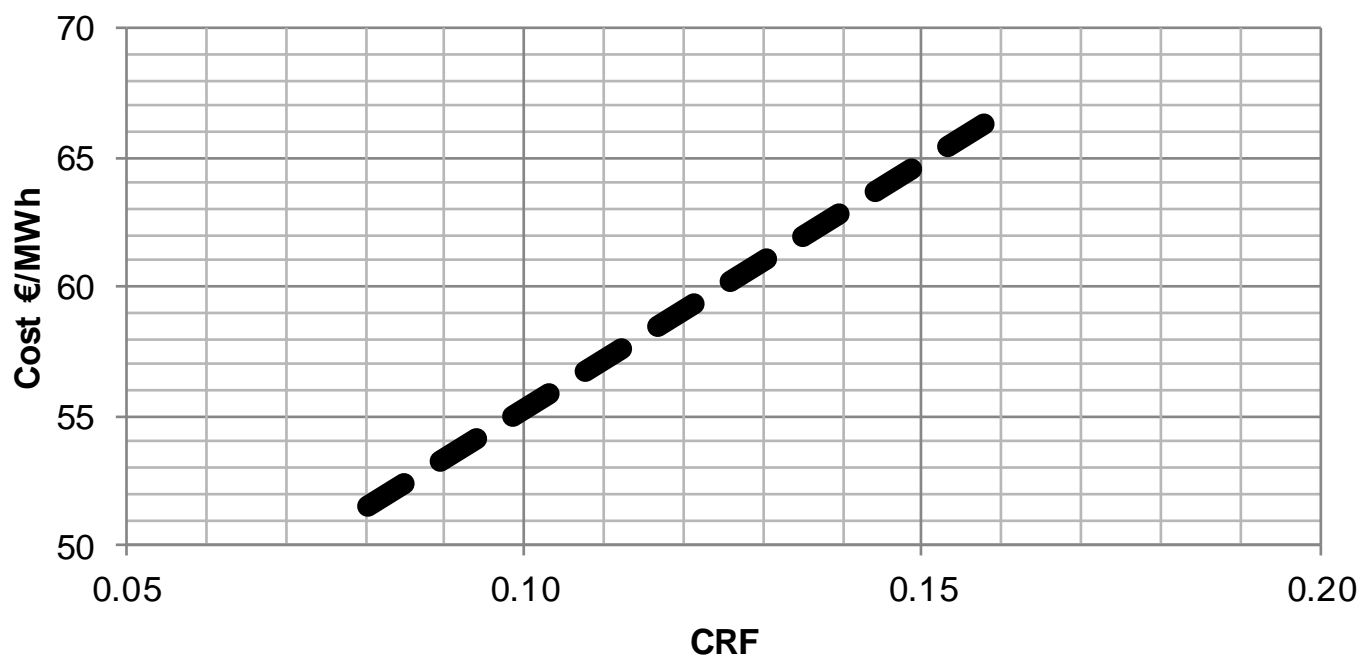




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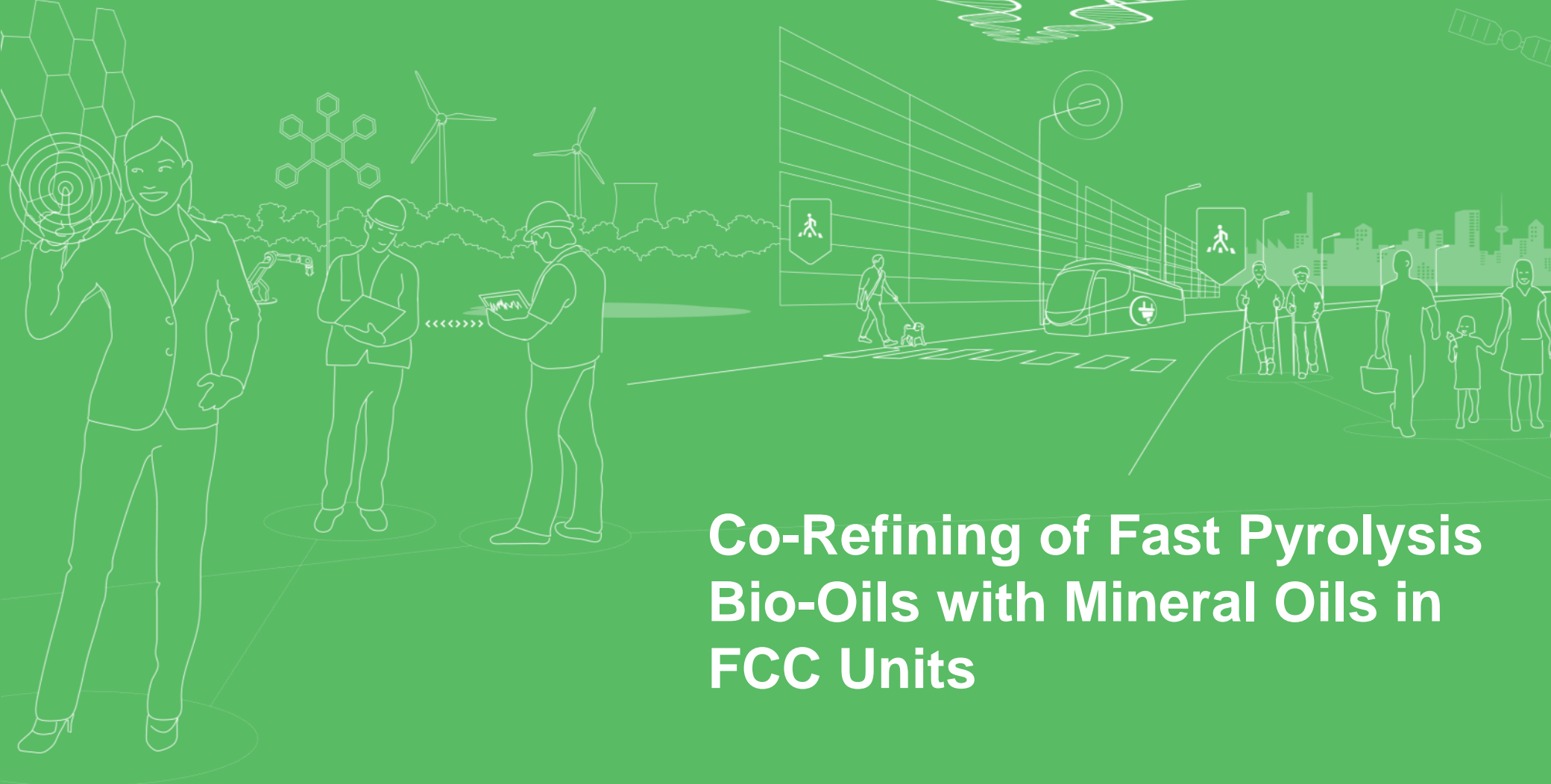
Bio-Oil Production Cost as a Function of Capital Recovery Factor





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Co-Refining of Fast Pyrolysis Bio-Oils with Mineral Oils in FCC Units

Background

- Vegetable oils have been used especially in Europe to produce a renewable diesel oil substitutes (biodiesel, FAME). Due to their long side carbon chains and absence of aromatic rings, these oils can also be processed in a fluid catalytic cracking unit (FCC) to produce gasoline or light olefins.
- Interest of using of fast pyrolysis bio-oils in co-refining was also considered. Co-processing using hydrodeoxygenated (HDO) pyrolysis-oils were successfully co-processed with vacuum gasoil (VGO) in a laboratory scale fluid catalytic cracking (FCC) unit to bio-fuels*. However, it is known that full HDO for pyrolysis oils is expensive, and also technically challenging (see later).
- The following step was to try catalytic fast pyrolysis oil for FCC co-refining. Results were quite encouraging, and FCC yields were similar to those only with VGO feed**. However, liquid yields in catalytic pyrolysis are considerably lower than in thermal pyrolysis, and therefore there is a concern of the overall carbon yield.

* a) F. De Miguel Mercader, M.J. Groeneveld, S.R.A. Kersten, N.W.J. Way, C.J. Schaverien, J.A. Hogendoorn, *Applied Catalysis B: Environmental*, 96 (2010), pp. 57–66, b) G. Fogassy, N. Thegarid, G. Toussaint, A.C. van Veen, Y. Schuurman, C. Mirodatos, *Applied Catalysis B: Environmental*, 96 (2010), pp. 476–486

** Agblevor, F. A.; Mante, O.; Abdoulmoumine, N., McClung, R.; Nourredine Abdoulmoumine. *Production of Stable Biomass Pyrolysis Oils Using Fractional Catalytic Pyrolysis. Energy Fuels* 2010, 24, 4087–4089

Status of Co-Refining

- Sometime around 2010 Petrobras became interested in fast pyrolysis. This was around the same time KiOR was generating much interest in the US (see later).
- First Petrobras did co-refining tests with BTG oil. The first results on these tests were published early 2015*. There was also a slide set presented at DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review**.
- The most extensive article so far on this alternative was recently published by Petrobras and NREL***. A 200 kg/h FCC pilot as employed for the co-refining tests. Petrobras reports unlike earlier publications that co-refining with thermal fast pyrolysis bio-oil is possible as such, provided that a large enough scale is used, and feeding is done correctly.
- The scheme and the unit applied are shown on next two pages. Pictures are from Pinho 2017.

* *Andrea de Rezende Pinho, Marlon B.B. de Almeida, Fabio Leal Mendes, Vitor Loureiro Ximenes, Luiz Carlos Casavechia, Co-processing raw bio-oil and gasoil in an FCC Unit, Fuel Processing Technology, Volume 131, March 2015, Pages 159-166*

** http://www.energy.gov/sites/prod/files/2015/04/f21/thermochemical_conversion_chum_242303.pdf

*** *Andrea de Rezende Pinho, Marlon B.B. de Almeida, Fabio Leal Mendes, Luiz Carlos Casavechia, Michael S. Talmadge, Christopher M. Kinchin, Helena L. Chum, Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production, Fuel, Volume 188, 15 January 2017, Pages 462-473*



Petrobras, US DoE, Ensyn

- The collaboration is presented in following slides. The slides are from Helene Chum's (NREL) presentation http://www.energy.gov/sites/prod/files/2015/04/f21/thermochemical_conversion_chum_242303.pdf
- Total reported costs are about 2.5 M\$.
- The economics analysis is presented in two slides. Not surprisingly, pyrolysis bio-oil cost have the largest impact on the profitability of co-refining.
- The price shown on slide 39 (1.43 \$/gal) for bio-oil corresponds to about 64 to 74 €/MWh depending of the heating value assumed for bio-oil.

Quad Chart Overview





Timeline

Actual Start Date	February, 2013
End Date	September, 2015
Overall % Complete	75%
NREL % Complete	50%

Budget

	Total Costs FY10 to FY12	FY 13 Costs	FY 14 Costs to Q1 FY15	Total Planned Funding FY15-End Date
<u>DOE Funded BETO</u>		\$41K	\$58K	\$265K
<u>EERE Intl.</u>	\$37K	\$71K	\$56K	\$250K

Project Cost Share

1. Petrobras \$1,976K 
2. Ensyn Corp. \$100 K 

Barriers

Addressed:

- Tt-S. Petroleum Refinery Integration of Bio-Oil
- Tt-R. Process Integration
- Tt-K. Product Finishing

Other:

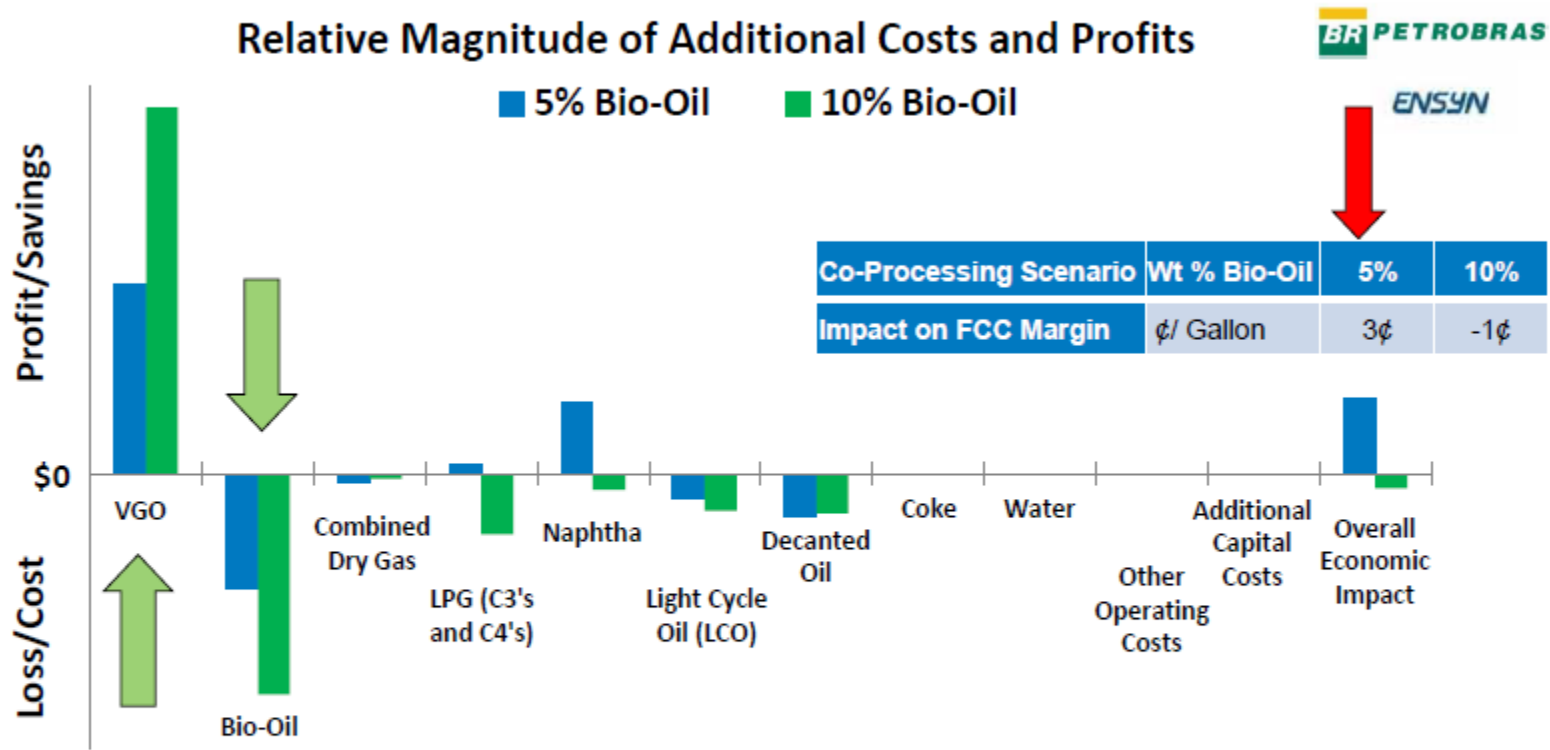
- Commercial Suppliers of Bio-oils
- Direct Bio-Oil Coprocessing in FCC deemed not possible because of coke formation


Partners


- Petrobras R&D, CENPES, Rio de Janeiro, RJ
- Petrobras SIX facility, Sao Matheus do Campo, PR, Brazil
- NREL – National Bioenergy Center, Alternative Fuels and Strategic Energy Analysis
- Ensyn Corp. and partners, principally Fibria Celulose, Brazil

4 : 1 partners : DOE funding

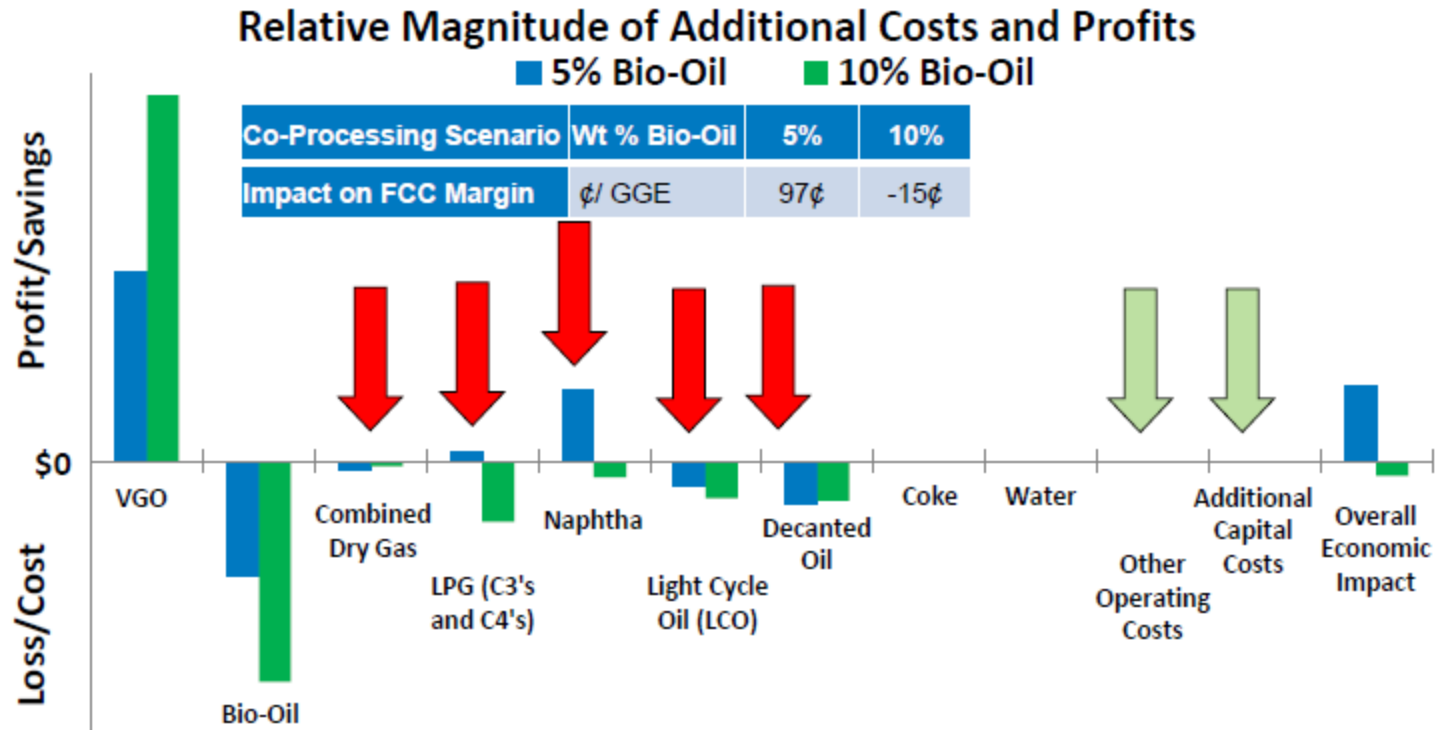
3 – Accomplishments and Results



 **Overall blending has a positive impact on profits for 5% bio-oil, slightly negative for 10% Bio-oil. Process not optimized**

 **Most significant impact on profitability is the cost of feed to the FCC Unit**

3 – Accomplishments and Results



Value of products have less significant impact relative to feed cost, but is significant relative to the overall economic impact

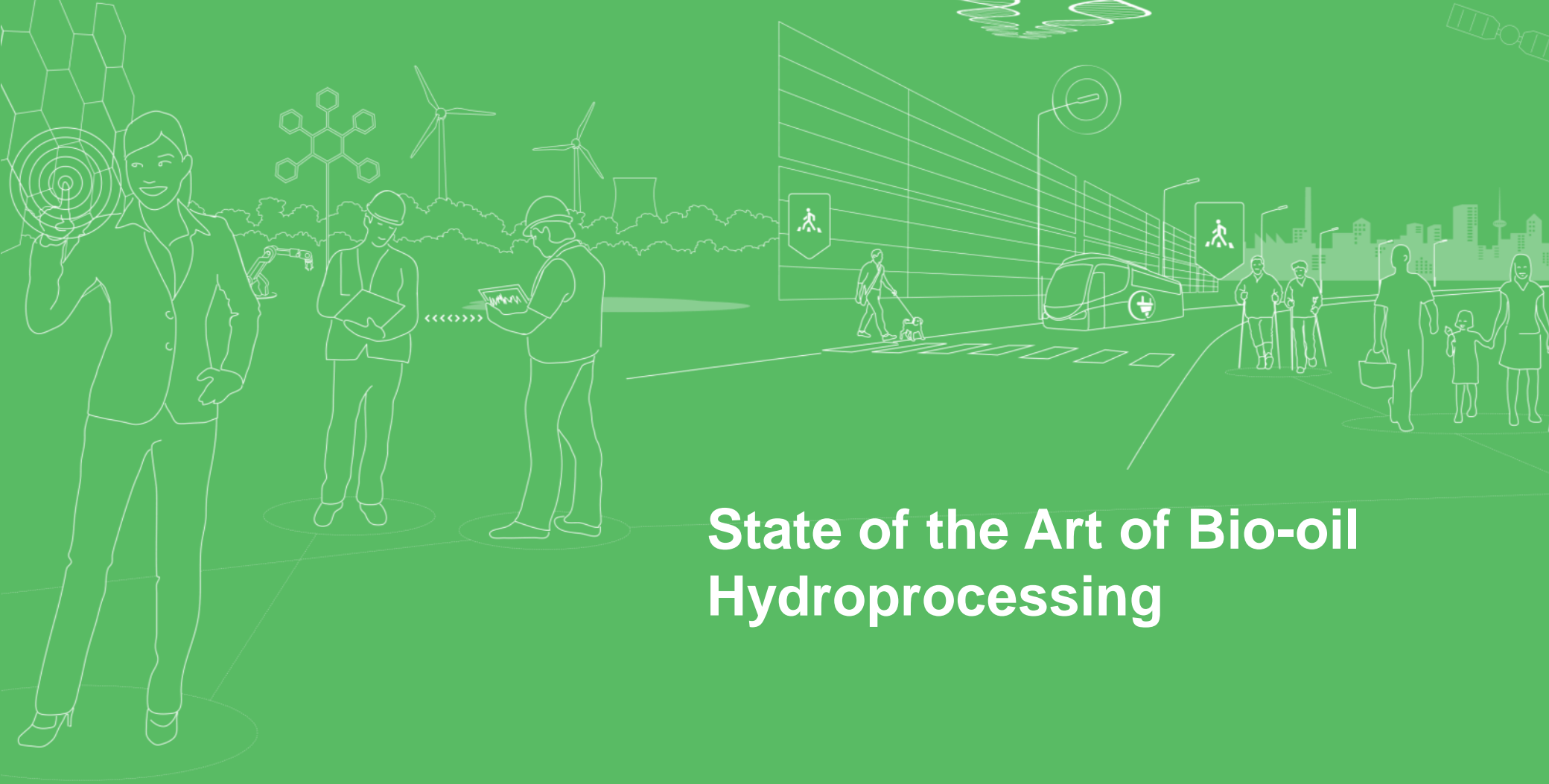


Additional capital and operating costs are insignificant compared to the value of VGO, bio-oil, and FCC products



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State of the Art of Bio-oil Hydroprocessing



Pyrolysis bio-oil hydrodeoxygenation

- Baker and Elliott* reported in 1988 of a method for treating bio-oil through hydroprocessing, which was similar to the catalytic hydrotreating of mineral oils.
- Since then, considerable efforts has been devoted to this aim**.
- In addition to several research organization and universities, especially UOP has been active in developing the technology***.
- However, the largest experiments in public domain are continuously in bench-scale.
- Two examples of the most successful reported developments are presented on following 6 slides.

* Baker, E.G. and D.C. Elliott, *Catalytic upgrading of biomass pyrolysis oils. Research in Thermochemical Biomass Conversion*, ed. A.V. Bridgwater and J.L. Kuester. 1988, Barking Essex: Elsevier Appl Sci Publ Ltd. 883-895

** Elliott DC (2007) *Historical developments in hydroprocessing bio-oils. Energy Fuels* 21(3):1792–1815

*** for example Baird, et al., *Methods and apparatuses for deoxygenating biomass-derived pyrolysis oil. US 9,163,181* October 20, 2015.



Pacific Northwest National Laboratory, PNNL (Richland, Wash)

- PNNL has been pioneering the multi-step HDO of pyrolysis bio-oil.
- Hydroprocessing of bio-oil has always caused plugging of the reactor at one point due to the reactivity of bio-oil.
- In 2016 PNNL reported* a continuous 1440 h operation. However, note that deactivation of the 1st zone bed still occurred and it required replacement after about 750 h operation.

* Mariefel V. Olarte, et al., *Stabilization of Softwood-Derived Pyrolysis Oils for Continuous Bio-oil Hydroprocessing*. *Top Catal* (2016) 59:55–64



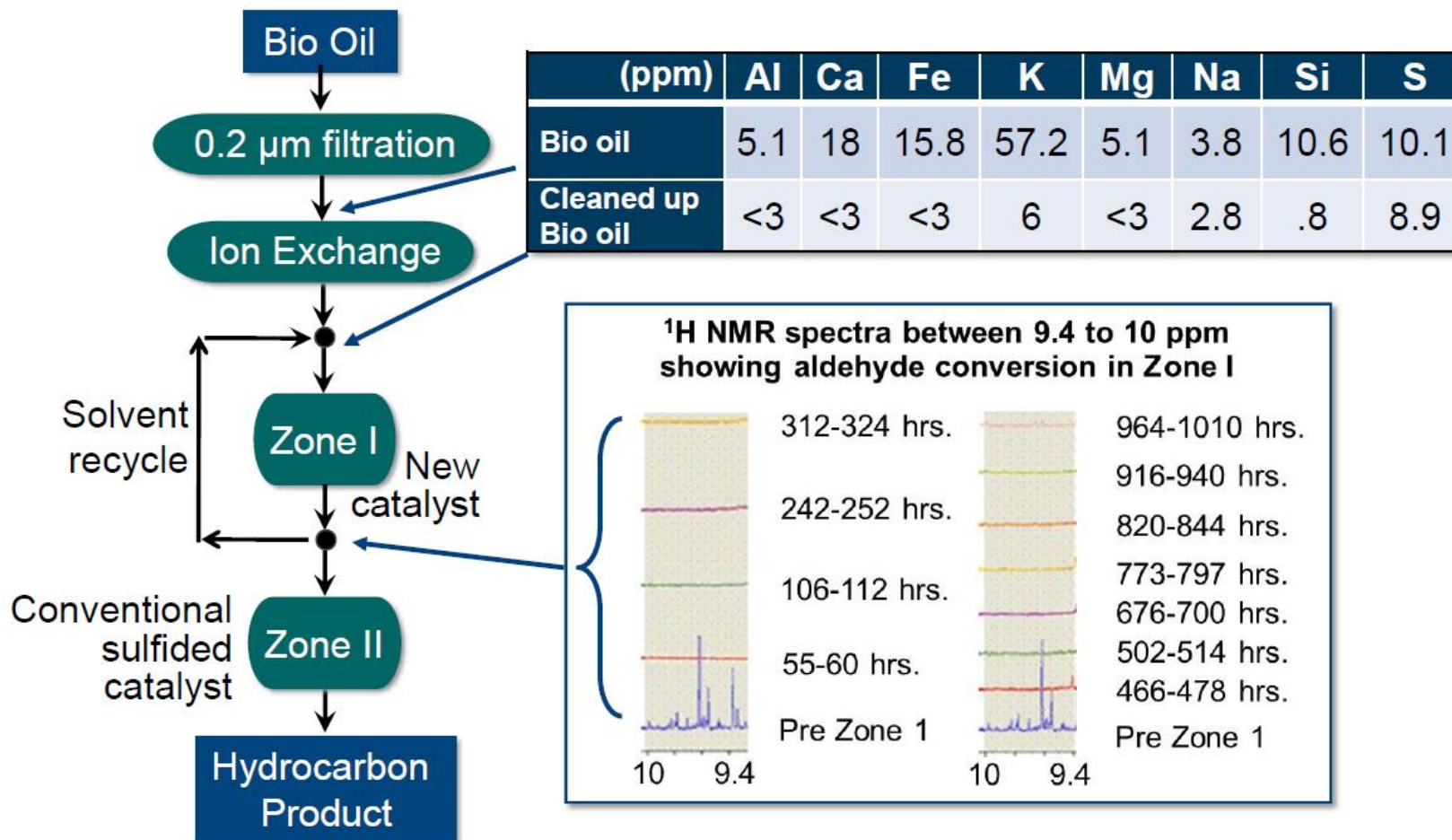
Battelle Memorial Institute (Ohio)

- Another approach for continuous HDO of pyrolysis bio-oil was employed by Zia Abdullah*: Thorough filtration of bio-oil, followed by ion-exchange, followed by two-stage hydroprocessing with an oil recycle and an improved new catalyst in the first stage (next slide).
- Over 1 000 h of operation was achieved, which was the goal set by the DOE (slide after).

* http://www.energy.gov/sites/prod/files/2015/04/f21/thermochemical_conversion_abdullah_231401.pdf

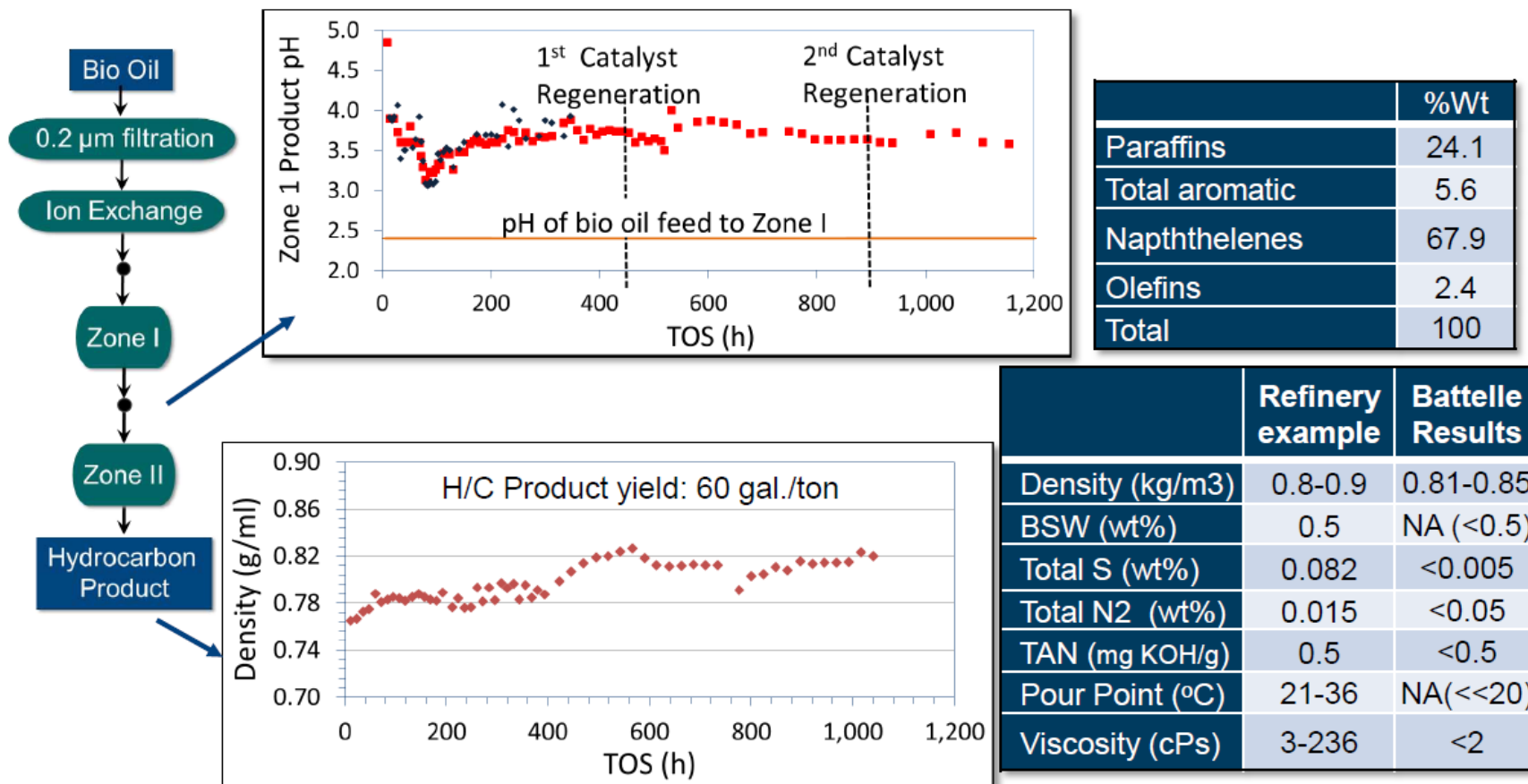
3 – Technical Accomplishments/Progress/Results

Task D : Developed a New Process For Bio oil Hydrotreatment



3 – Technical Accomplishments/Progress/Results

Task F, G : Approximately 1,200 hrs. TOS Achieved in Zone I, and as of March 17, 2015, 1,060 hrs. Achieved in Zone II





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Summary

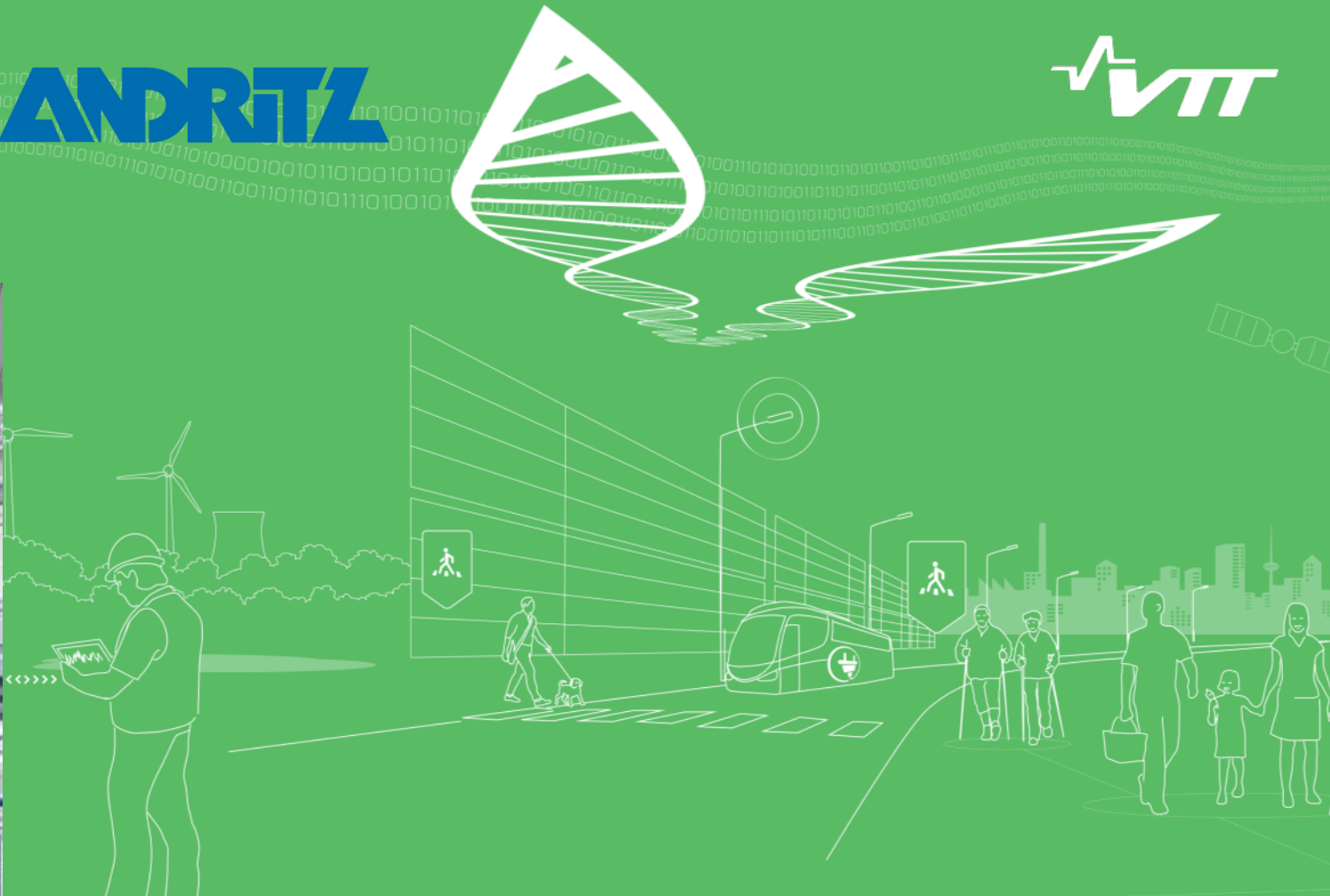
- Two factors have been reported by PNNL to enable continuous HDO of pyrolysis bio-oil: (1) a bio-oil pretreatment process prior to the two-temperature reactor, and (2) a robust commercial catalyst for the high temperature zone reactor.
- Pretreatment liquid hourly space velocity (LHSV) was typically 0.5 L bio-oil/ (L catalyst bed-h) while an overall full hydroprocessing LHSV was typically around 0.1 L bio-oil/(L catalyst bed-h) in the PNNL work.
- Battelle was successful in HDO by thorough filtration and ion-exchange of the oil, followed by two stage hydroprocessing. Hourly space velocities were not reported.

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VTT



Catalytic Fast Pyrolysis

Paasikallio, Ville. 2016. Bio-oil production via catalytic fast pyrolysis of woody biomass, VTT and Aalto University. 166 p. VTT Science; 137 ISBN 78-951-38-8466-6; 978-951-38-8465-9 <http://www.vtt.fi/inf/pdf/science/2016/S137.pdf>

- The quality of the bio-oil can be improved using a variety of catalytic processes. One such technology is catalytic fast pyrolysis (CFP), which integrates a catalytic vapor-phase upgrading step directly into a fast pyrolysis process itself.
- CFP is most often carried out using acidic zeolite catalysts, which are capable of removing oxygen from the pyrolysis vapors in the form of carbon oxides and water. Because both carbon and hydrogen are lost together with the oxygen, the quality of bio-oil improves at the expense of the yield.
- Circulating fluidized bed reactors with continuous catalyst regeneration provide a convenient technological platform for CFP. The effect of coke-induced reversible deactivation is effectively negated, and the focus can be shifted to process performance and catalyst long-term stability. The latter factor is considered to be one of the key questions for CFP. It was shown in this thesis that the combination of biomass-derived inorganic contaminants and severe reaction/regeneration conditions cause irreversible changes in the catalyst structure and properties, which in turn reflects in the quality of the bio-oil.
- The results of this thesis also highlight the diverse overall character of the CFP products. The partially upgraded bio-oil product is accompanied by a separate aqueous liquid with varying amounts of dissolved organics. Thus, efficient utilization of the CFP products would very likely entail more than one valorization approach.



KiOR

- KiOR was the first effort to scale-up biomass catalytic pyrolysis
- The attempt failed due to a number of reasons, which are explained in a series of articles in Biofuels Digest <http://www.biofuelsdigest.com/bdigest/?s=kior>.
- The next page lists references to this series of five articles in Biofuels Digest
- The following slide summarises the reasons of failure by the State of Mississippi

Detailed description of the KiOR history

- <http://www.biofuelsdigest.com/bdigest/2016/05/17/kior-the-inside-true-story-of-a-company-gone-wrong/>
- <http://www.biofuelsdigest.com/bdigest/2016/05/18/kior-the-inside-true-story-of-a-company-gone-wrong-part-2/>
- <http://www.biofuelsdigest.com/bdigest/2016/08/03/the-inside-true-story-of-a-company-gone-wrong-part-3-youve-cooked-the-books/>
- <http://www.biofuelsdigest.com/bdigest/2016/09/18/kior-the-inside-true-story-of-a-company-gone-wrong-part-4-the-year-of-living-disingenuously/>
- <http://www.biofuelsdigest.com/bdigest/2016/11/24/kior-the-story-of-a-company-gone-wrong-part-5-the-collapse/9/>

KiOR – State of Mississippi on the specific failures of the company’s technology and the cover-up*

1. KiOR’s total process yields were not high enough to render the Company profitable.
2. KiOR’s catalyst costs, catalyst replacement rate and capacity creep all contributed to render the Company unprofitable.
3. KiOR did not make a high quality crude oil, but instead made a biocrude that was high in oxygen and acids which made the biocrude difficult to refine within the standard equipment of major oil companies.
4. KiOR had been informed by [Catchlight Energy] and other major oil companies that they were unable and unwilling to refine the Company’s biocrude in quantities that the parties found acceptable.
5. Due to its inability to convince a major oil company to refine its biocrude, KiOR was forced to construct and operate its own refinery in Columbus. These additional costs had not been included in the Company’s financial modeling and projections.

* <http://www.biofuelsdigest.com/bdigest/2016/11/24/kior-the-story-of-a-company-gone-wrong-part-5-the-collapse/9/>



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Future developments



Development of bio-oil co-refining and scale-up of new technologies

- Road map for new developments is shown on the next page
- This road map is roughly national, however, it is based on industrial development in the technology area globally
- It is therefore believed it may be considered fairly global concerning the technologies employed
- Please note that HTL (hydrothermal liquefaction, high pressure liquefaction) is also shown as HTL bio-oils may also be employed in co-refining

Development of bio-oil co-refining

2014-6

- Industrial plants by Fortum, BTG, Ensyn
- Petrobras co-refining 2013-14
- UOP presentation 2014

ROADMAP

Stage 1 – 2016-8

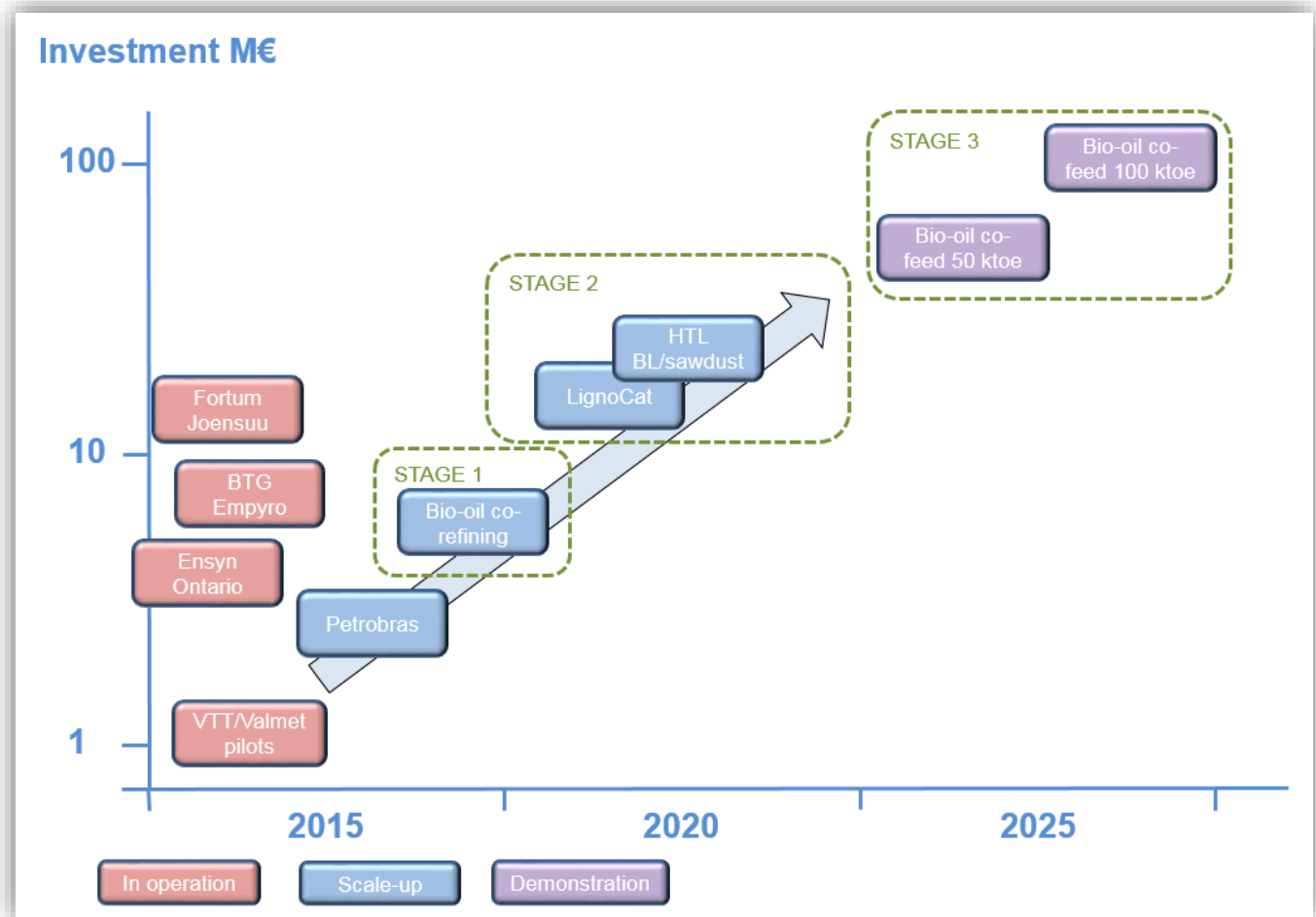
- Different feeds in pilot and co-refining

Stage 2 – 2020->

- HTL, catalytic pyrolysis
- Industrial co-refining and new industrial pilots

Stage 3 – 2025->

- Deployment of new industrial units





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Markets



Pyrolysis bio-oil standardisation

- An overview of standardization committees* under CEN and ISO for solid, liquid and gaseous biofuels is shown on next page.
- European standard for fast pyrolysis bio-oil (FPBO) use in boilers has been in preparation since 2014. The EN standard 16900 is almost finalized (October 2016), and planned to be published in the beginning of 2017*.
- Two different grades are specified. In addition to the quality requirements and test methods for FPBOs, further instructions on storage, sampling, and materials compatibility are given.
- Working group 41 is also drafting a technical report (CEN/TR) for the use of FPBO in stationary internal combustion engines.

* <http://task34.ieabioenergy.com/wp-content/uploads/2016/10/Issue-39-Task-34-Newsletter-Oct-2016.pdf>

Table 1: Overview of standardisation committees under CEN and ISO for solid, liquid and gaseous biofuels.

Committee	Name	Remarks
CEN/TC 335	Solid biofuels	Standardisation work has finished and new standards, which supersede these standards, will be published under ISO/TC 238.
ISO/TC 238	Solid biofuels	Standardization of terminology, specifications and classes, quality assurance, sampling and sample preparation and test methods in the field of raw and processed materials originating from arboriculture, agriculture, aquaculture, horticulture and forestry to be used as a source for solid biofuels. Vienna agreement ¹ to be followed and standards will be published in Europe as EN ISO standards.
CEN/TC 019	Petroleum products, lubricants and related products	WG 41 to develop quality specifications for pyrolysis products for boilers and stationary internal combustion engines
CEN/TC 343	Solid recovered fuels	Solid recovered fuels prepared from non-hazardous waste. Work is finished and new standards will be published under ISO/TC 300.
ISO/TC 300	Solid recovered fuels	Elaboration of standards and other deliverables on solid recovered fuels prepared from non-hazardous waste to be utilised for energy recovery in waste incineration or co-incineration plants or in industrial processes (like cement manufacturing), excluding fuels that are included in the scope of ISO/TC 238.
CEN/TC 383	Sustainably produced biomass for energy applications	Sustainability principles, criteria and indicators including their verification and auditing schemes, for as a minimum, but not restricted to, biomass for energy applications. This includes GHG emission and fossil fuel balances, biodiversity, environmental, economic and social aspects and indirect effects within each of the aspect, include only sustainability of biofuels and bioliquids for energy applications.
ISO/TC 248	Sustainability criteria for bioenergy	Sustainability criteria for production, supply chain and application of bioenergy. The work has finished and 4 standards published.
ISO/TC 255	Biogas	Standardization in the field of biogas
CEN/TC 408	Natural gas and biomethane for use in transport and biomethane for injection in the natural gas grid	Standardization of specifications for natural gas and biomethane as vehicle fuel and of biomethane for injection in the natural gas grid, including any necessary related methods of analysis and testing. Production process, source and the origin of the source are excluded.

¹Vienna agreement signed in 1991 was drawn up with the aim of preventing duplication of effort and reducing time when preparing standards. As a result, new standards projects are jointly planned between CEN and ISO. ISO standards will be published in Europe as EN ISO standards and voting of different phase will carried out parallel.



Bio-oil properties included in the standard*

Table 2: Property requirements and test methods for fast pyrolysis bio-oils for boiler use (FprEN 16900, June 2016)*

Property	Unit	Test Method
Net calorific value as received ^a	MJ/kg	DIN 51900-3
Water content, on wet basis	%(m/m)	ASTM E203
pH		ASTM E70
Density at 15 °C	kg/dm ³	EN ISO 12185
Pour point	°C	ISO 3016
Nitrogen content	%(m/m) (d.b. ^b)	ASTM D5291

^a Net calorific value as received is calculated from the gross calorific value according to DIN 51900-1.
^b d.b. is on dry basis.

Threshold values of Table are not published because of CEN copyright reasons.

Emission and burner dependent property requirements and test methods for fast pyrolysis bio oil for boiler use (FprEN 16900) for Grade 1 and Grade 2^{*}.

Property	Test method	Unit
Kinematic viscosity at 40 °C	EN ISO 3104	mm ² /s
Sulfur content	EN ISO 20846	%(m/m), d.b. ^a
Solids content	ASTM D7579	%(m/m)
Ash content	EN ISO 6245	%(m/m), d.b. ^a
Na, K, Ca, Mg	EN 16476	%(m/m) d.b. ^a

^a d.b. on dry basis

Threshold values for Grade 1 and Grade 2 in Table are not published because of CEN copyright reasons.

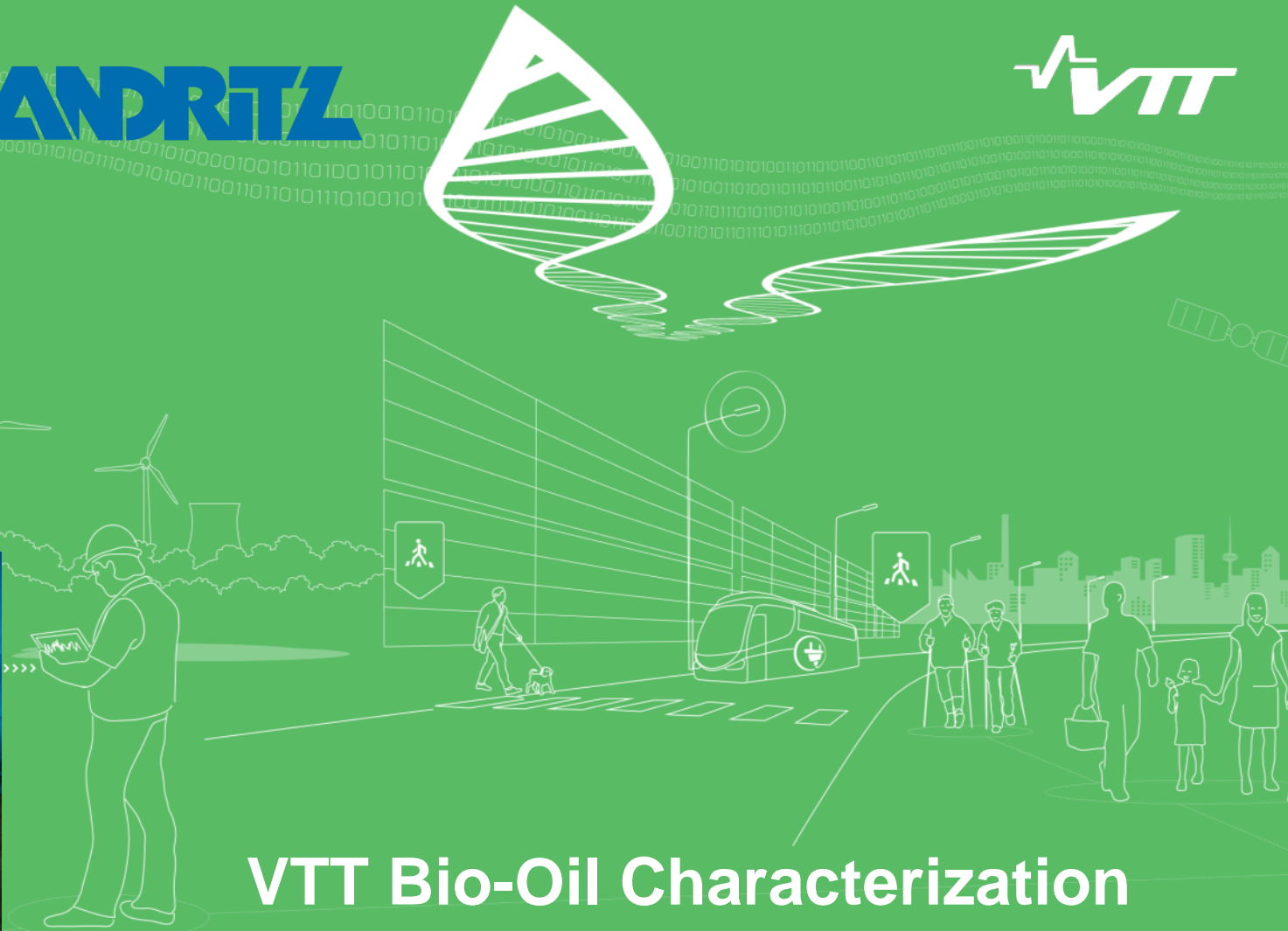
* <http://task34.ieabioenergy.com/wp-content/uploads/2016/10/Issue-39-Task-34-Newsletter-Oct-2016.pdf>

best

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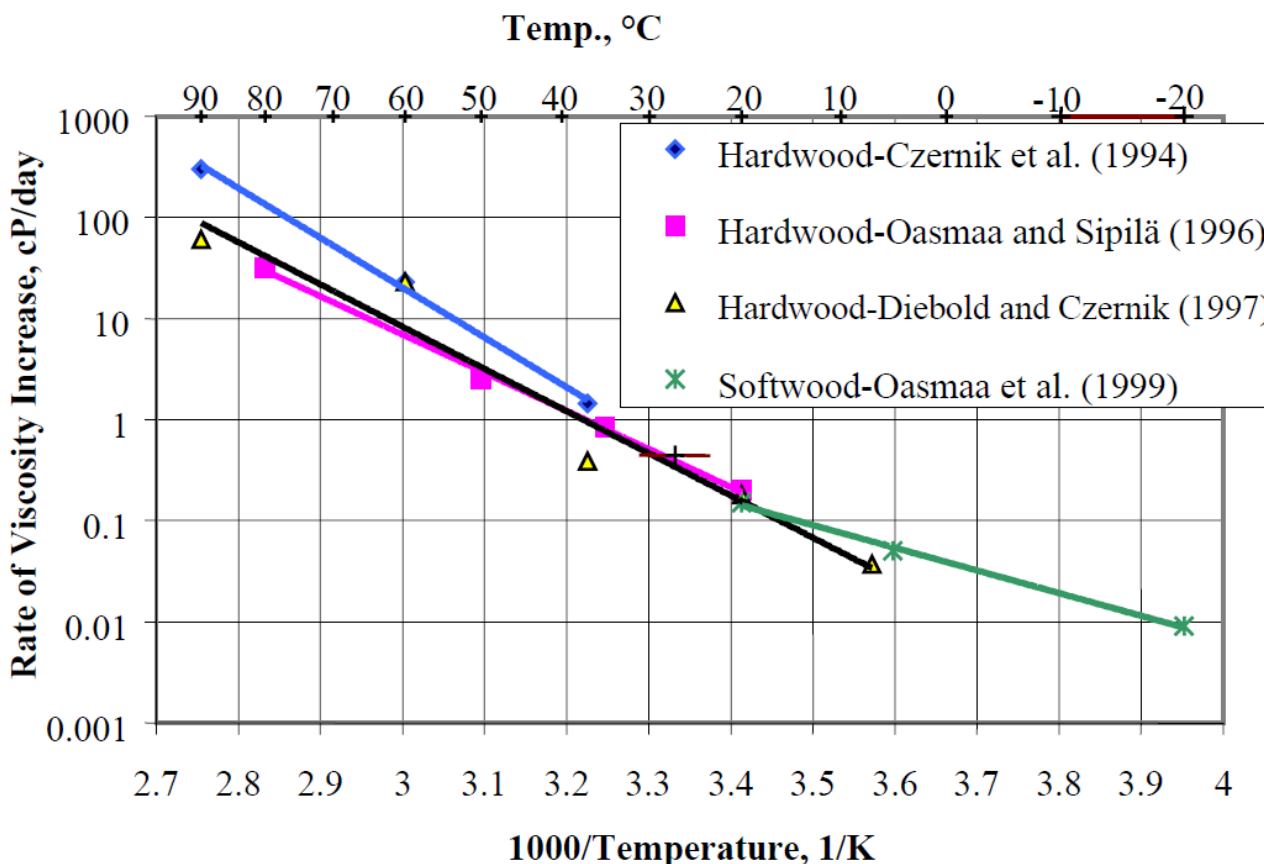


VTT Bio-Oil Characterization Built to Serve industrial Efforts and Standardization

VTT analytical services to pyrolysis bio-oil

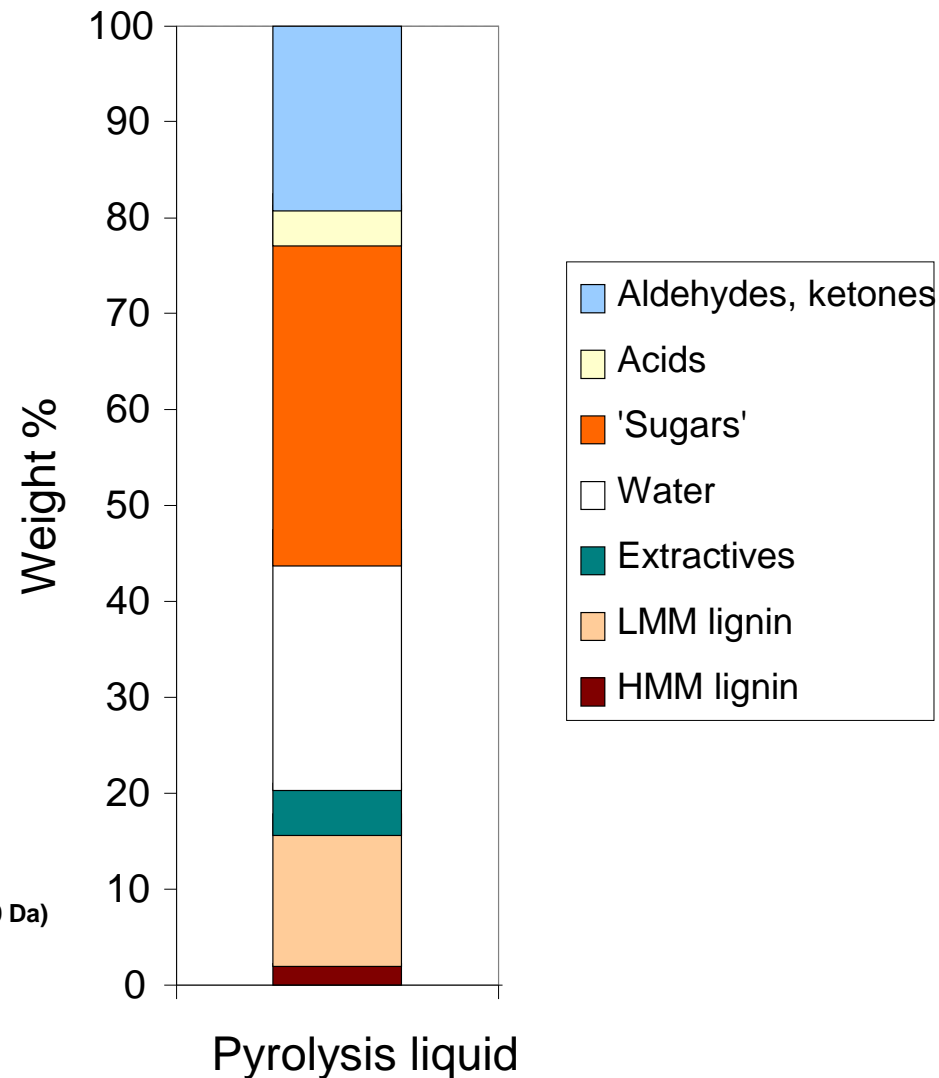
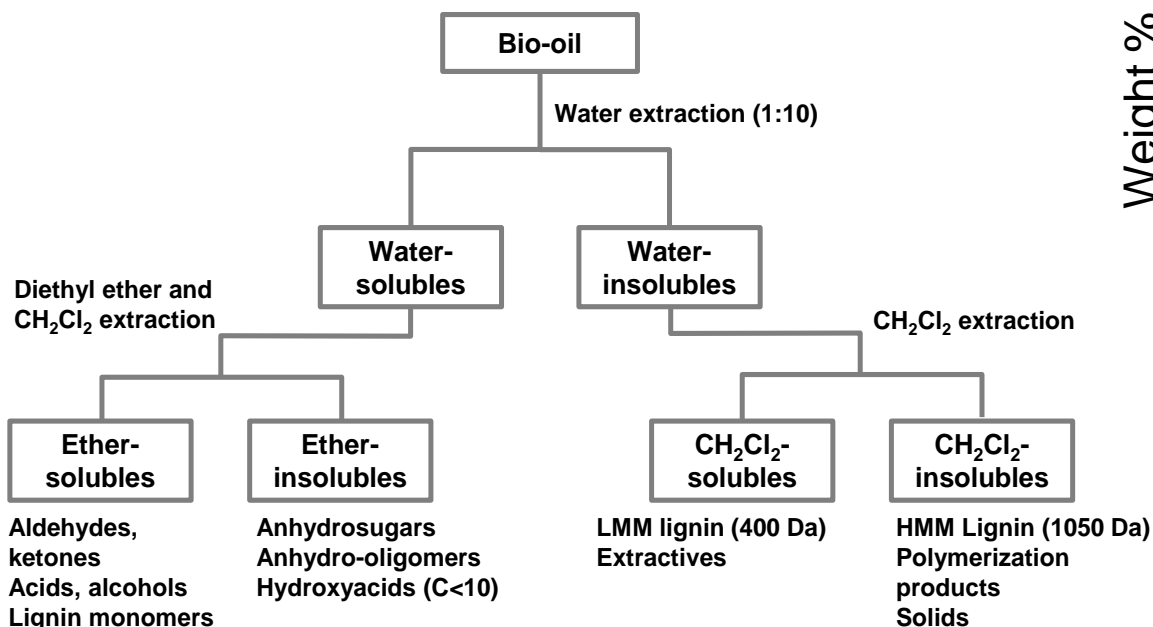
- VTT has published extensively on characterisation procedures for bio-oils. Many methods have been developed based on mineral oil standards, however, taken into consideration the specific properties of pyrolysis bio-oils.
- Some important properties of pyrolysis bio-oils are shown on next pages.
- One important reference:
 - Oasmaa, Anja, Peacocke, Cordner. A guide to physical property characterisation of biomass-derived fast pyrolysis liquids. A guide. VTT Publications: 731, VTT, Espoo, 2010, 79 p. + app. 46 p. ISBN 978-951-38-7384-4
<http://www.vtt.fi/inf/pdf/publications/2010/P731.pdf>
- Selected other references concerning development of fast pyrolysis at VTT 2011-16 are on the last pages

Instability of Pyrolysis Bio-Oil - Effect of Time and Temperature on Viscosity Increase

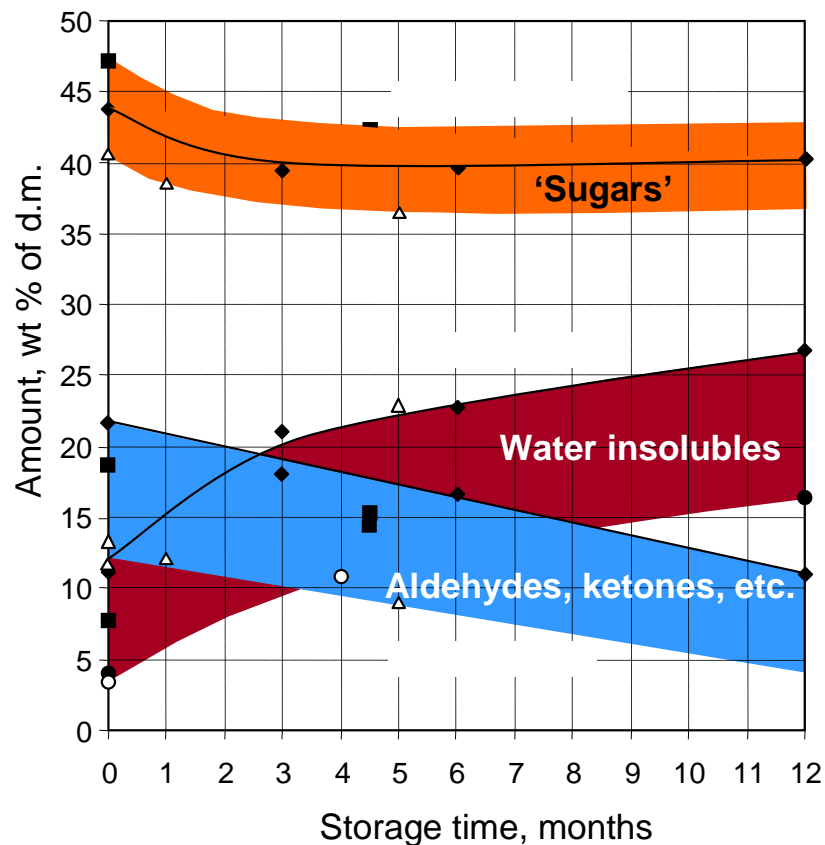


The instability of bio-oils can be observed as increased viscosity over time, particularly when heated

Fast Pyrolysis Bio-Oil Composition



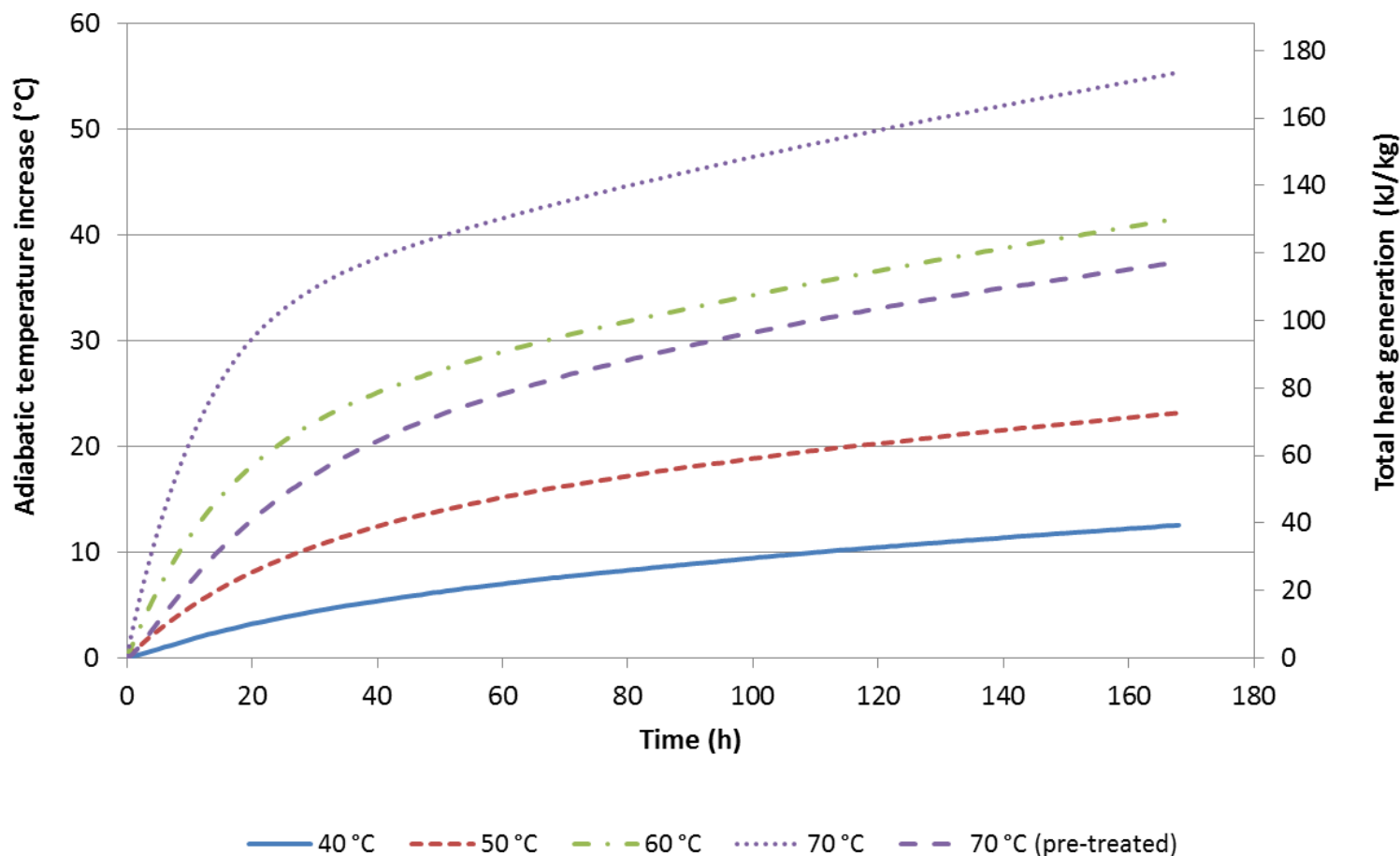
Reactivity of Bio-Oil Component Groups



- Increasing in bio-oil aging
 - Water
 - Viscosity
 - Water insoluble compounds (WIS)
 - High molecular weight fraction (HMM)
 - Molecular weight
- Decreasing in aging
 - Aldehydes and ketones (carbonyls)
 - "Sugars"

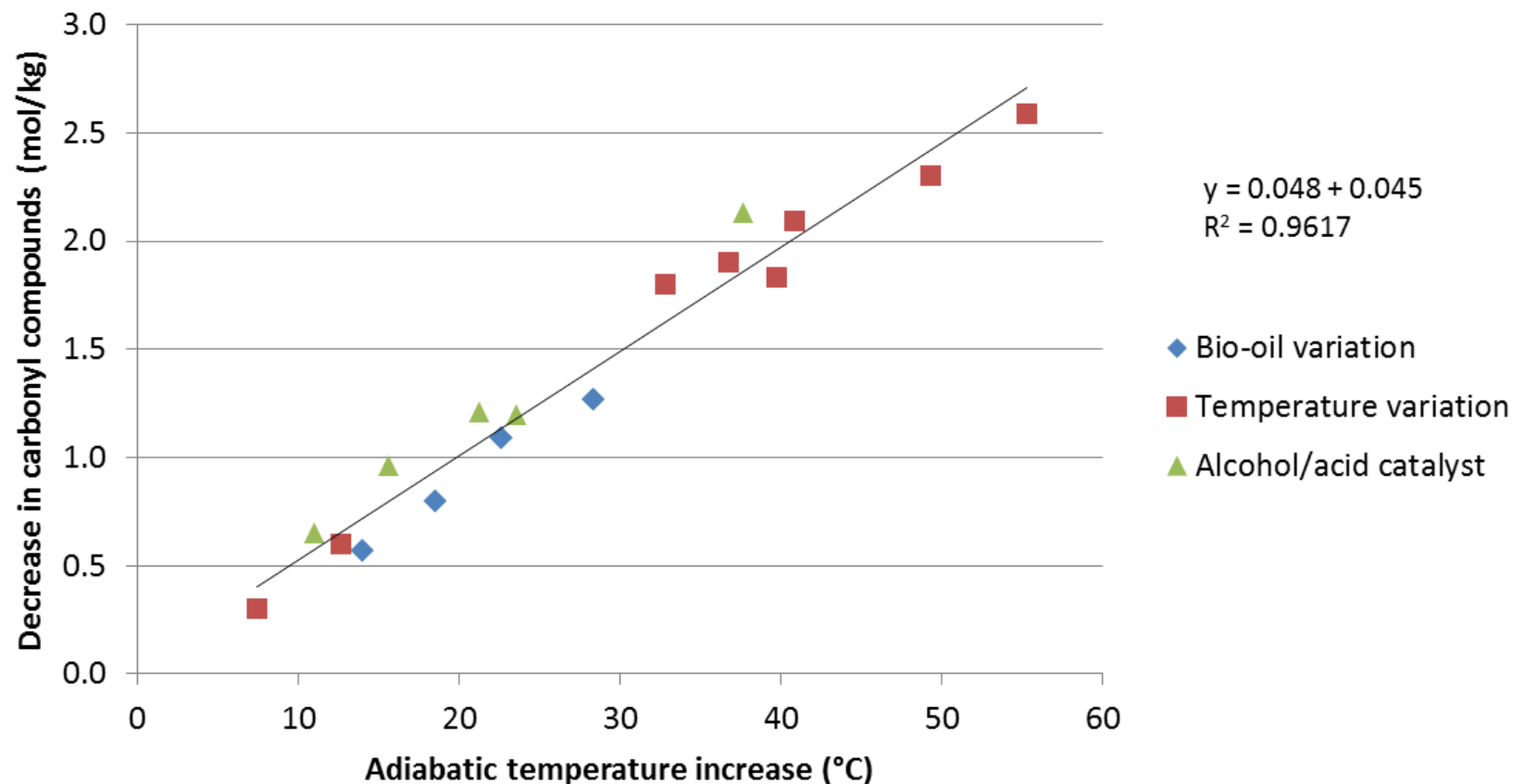
Oasmaa, Anja. 2003. Fuel oil quality properties of wood-based pyrolysis liquids. Academic dissertation. Jyväskylä, Department of Chemistry, University of Jyväskylä. 32 p. + app. 251 p. Research Report Series, Report; 99

Increase in Adiabatic Temperature (°C) and Total Heat Generation (kJ/kg) of Bio-Oil at Temperatures of 40-70 °C



Sundqvist, Tom, Solantausta, Yrjö, Oasmaa, Anja, Kokko, Lauri, Paasikallio, Ville. 2016. Heat generation during the aging of wood-derived fast-pyrolysis bio-oils: ACS Publications. Energy and Fuels, Vol. 30, No. 1, pp. 465-472

Correlation Between Adiabatic Temperature Increase (°C) and Decrease in Carbonyl Compounds (mol/kg) at Varying Ageing Conditions



Sundqvist, Tom, Solantausta, Yrjö, Oasmaa, Anja, Kokko, Lauri, Paasikallio, Ville. 2016. Heat generation during the aging of wood-derived fast-pyrolysis bio-oils: ACS Publications. Energy and Fuels, Vol. 30, No. 1, pp. 465-472



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- Sundqvist, Tom, Solantausta, Yrjö, Oasmaa, Anja, Kokko, Lauri, Paasikallio, Ville. 2016. Heat generation during the aging of wood-derived fast-pyrolysis bio-oils: ACS Publications. Energy and Fuels, Vol. 30, No. 1, pp. 465-472 doi:10.1021/acs.energyfuels.5b02544
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- Oasmaa, Anja, Sundqvist, Tom, Kuoppala, Eeva, Garcia-Perez, Manuel, Solantausta, Yrjö, Lindfors, Christian, Paasikallio, Ville. 2015. Controlling the phase stability of biomass fast pyrolysis bio-oils: American Chemical Society. Energy and Fuels, Vol. 29, No. 7, pp. 4373-4381 doi:10.1021/acs.energyfuels.5b00607
- Onarheim, Kristian, Solantausta, Yrjö, Lehto, Jani. 2015. Process simulation development of fast pyrolysis of wood using aspen plus : ACS Publications. Energy and Fuels, Vol. 29, No. 1, pp. 205-217 doi:10.1021/ef502023y

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- Sundqvist, T., Oasmaa, A., Koskinen, A.. 2015. Upgrading fast pyrolysis bio-oil quality by esterification and azeotrop: American Chemical Society. Energy and Fuels, Vol. 29, No. 4, pp. 2527-2534 doi:10.1021/acs.energyfuels.5b00238
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- Solantausta, Yrjö, Lehto, Jani, Oasmaa, Anja, Kjaldman, Lars. 2013. Status of fast pyrolysis bio-oil technologies. 21st European Biomass Conference and Exhibition, EU BC&E 2013, 3 – 7 June 2013, Copenhagen, Denmark. European Biomass Conference and Exhibition Proceedings. ISBN 978-88-89407-53-0
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- Oasmaa, Anja, Ranta, J., Källi, A., Solantausta, Yrjö, Sipilä, K., Lindfors, Christian. 2011. An emerging biofuel production chain: standardisation needs for fast pyrolysis bio-oil. 19th European Biomass Conference and Exhibition, EU BC&E 2011, 6 – 10 June 2011, Berlin, Germany
- Paasikallio, Ville, Agblevor, F., Oasmaa, Anja, Lehto, Jani, Lehtonen, Juha. 2013. Catalytic pyrolysis of forest thinnings with ZSM-5 catalysts: Effect of reaction temperature on bio-oil physical properties and chemical composition: American Chemical Society. Energy and Fuels, Vol. 27, No. 12, pp. 7587 – 7601 doi:10.1021/ef401947f
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- Paasikallio, Ville, Lindfors, Christian, Lehto, Jani, Oasmaa, Anja, Reinikainen, Matti. 2013. Short vapour residence time catalytic pyrolysis of spruce sawdust in a bubbling fluidized-bed reactor with HZSM-5 catalysts: Springer. Topics in Catalysis, Vol. 56, No. 9-10, pp. 800 – 812 doi:10.1007/s11244-013-0037-y
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- Oasmaa, Anja, Korhonen, Jaana, Kuoppala, Eeva. 2011. An approach for stability measurement of wood-based fast pyrolysis bio-oils: ACS Publications. Energy and Fuels, Vol. 25, No. 7, pp. 3307-3313 doi:10.1021/ef2006673
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- Oasmaa, Anja, Peacocke, Cordner. 2010. A guide to physical property characterisation of biomass-derived fast pyrolysis liquids. A guide. VTT Publications: 731, Espoo, VTT, 79 p. + app. 46 p. ISBN 978-951-38-7384-4 <http://www.vtt.fi/inf/pdf/publications/2010/P731.pdf>
- Oasmaa, Anja, Elliott, Douglas, C., Korhonen, Jaana. 2010. Acidity of Biomass Fast Pyrolysis Bio-oils: American Chemical Society. Energy and Fuels, Vol. 24, pp. 6548-6554 doi:10.1021/ef100935r
- Oasmaa, Anja, Kuoppala, Eeva, Ardiyanti, A., Venderbosch, R.H., and Heeres, H.J.. 2010. Characterization of Hydrotreated Fast Pyrolysis Liquids: American Chemical Society. Energy and Fuels, Vol. 24, No. 9, pp. 5264-5272 doi:10.1021/ef100573q
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