



VTT Technical Research Centre of Finland

## Historical Review on VTT Fast Pyrolysis Bio-oil Production and Upgrading

Oasmaa, Anja; Lehto, Jani; Solantausta, Yrjö; Kallio, Sirpa

*Published in:*  
Energy & Fuels

*DOI:*  
[10.1021/acs.energyfuels.1c00177](https://doi.org/10.1021/acs.energyfuels.1c00177)

Published: 01/01/2021

*Document Version*  
Publisher's final version

*License*  
CC BY

[Link to publication](#)

*Please cite the original version:*  
Oasmaa, A., Lehto, J., Solantausta, Y., & Kallio, S. (2021). Historical Review on VTT Fast Pyrolysis Bio-oil Production and Upgrading. *Energy & Fuels*, 35(7), 5683–5695. <https://doi.org/10.1021/acs.energyfuels.1c00177>

VTT  
<https://www.vttresearch.com>

VTT Technical Research Centre of Finland Ltd  
P.O. box 1000  
FI-02044 VTT  
Finland

By using VTT Research Information Portal you are bound by the following Terms & Conditions.

I have read and I understand the following statement:

This document is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of this document is not permitted, except duplication for research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered for sale.

# Historical Review on VTT Fast Pyrolysis Bio-oil Production and Upgrading

Anja Oasmaa,\* Jani Lehto, Yrjö Solantausta, and Sirpa Kallio



Cite This: *Energy Fuels* 2021, 35, 5683–5695



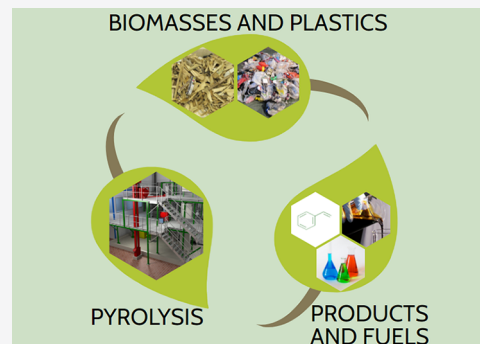
Read Online

ACCESS |

Metrics & More

Article Recommendations

**ABSTRACT:** The review summarizes VTT fast pyrolysis development efforts from the past 40 years. The experimental work has included a large variety of feedstocks (biomasses, wastes, oil shale, and plastic residues) and a variety of products (heating oils, refinery feeds, transportation fuels, and chemicals). As a result of the constant turbulence on fossil oil prices and changing regulatory framework, only a few renewable product alternatives are economically competitive. Plastic wastes appear to offer currently the most promising industrial opportunities.



## INTRODUCTION

This introduction aims to explain how the efforts of VTT Technical Research Centre of Finland, Ltd. related to biomass fast pyrolysis have evolved over the years. Although initially the aim of the organization was to replace mineral fuels by oils from biomass, the work has evolved into other feeds (wastes, oil shale, and plastic residues) and products (transportation fuels, refinery feeds, and chemicals) too.

The origin of this work at VTT may be traced back to the late 1970s, when alternatives for mineral oil products became of interest in most of the Organisation for Economic Co-operation and Development (OECD) countries. Synfuels through gasification were the first routes, which were studied in Finland and VTT in particular. Prof. Dan Asplund and Prof. Kai Sipilä were the original engines at VTT, and Sipilä remained at the helm related to fast pyrolysis up to the 2010s, among other areas. Other processing routes also raised interest internationally, and in the early 1980s, the International Energy Agency (IEA) Bioenergy Agreement set up a working group, in which Canada, Finland, Sweden, and the U.S.A. agreed to study direct liquefaction of biomass. Dr. Ralph Overend (representing Canada) and Dr. Don Stevens (representing the U.S.A.) were especially important movers of this project. By that time, the first pilot plants on fast pyrolysis (FP) and direct liquefaction/hydrothermal liquefaction (HTL) had already been operated in the U.S.A., with the first by Occidental Petroleum<sup>1</sup> and the second by the United States Department of Energy (U.S. DOE).<sup>2</sup> These efforts were not entirely successful, and simultaneously, the lower oil prices convinced the four countries to carry out together an assessment if a common test facility should be built. Three projects followed,<sup>3–10</sup> which compared

various alternative technologies for direct liquefaction of biomass. VTT was the Finnish representative for these projects.

Fast pyrolysis was assessed as the most promising biomass direct liquefaction route by the IEA working groups. The core people entering this conclusion were Dr. Björn Kjellström and Dr. Anders Östman (Sweden), Dr. Paterson McKeough and Dr. Yrjö Solantausta (VTT), David Beckman (Canada), and Dr. Douglas C. Elliott (the U.S.A.). These results and the contacts to the leading research and development (R&D) groups on this field, notably Dr. Donald Scott,<sup>11</sup> Jan Piskorz and their co-workers at the University of Waterloo (Canada) and Dr. Dietrich Meier at the Institute of Wood Chemistry (IWC, Germany), helped VTT to establish the first laboratory-scale fast pyrolysis reactor system at VTT by 1985.<sup>12</sup>

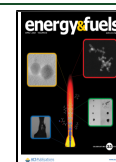
VTT R&D work of pyrolysis liquid production remained at modest laboratory scale for the next 10 years. Participation with international networks and collaboration with many European and North American partners were continued, and learning from the challenges related to the R&D was a necessary step for later industrial efforts.

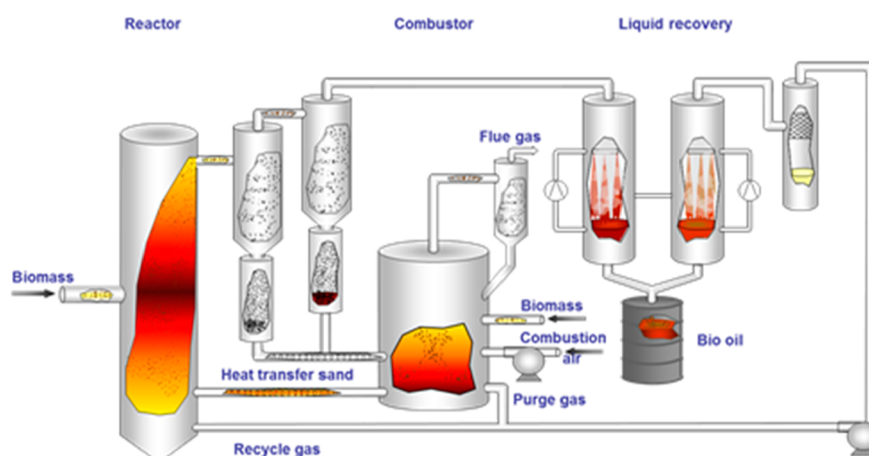
The networks lead by Prof. Tony Bridgwater were important venues to promote especially biomass fast pyrolysis. He led several projects on the topic funded by both IEA<sup>13</sup> (IEA Bioenergy sponsored Pyrolysis Activity, PYRA) and the

Received: January 25, 2021

Revised: March 2, 2021

Published: March 17, 2021





**Figure 1.** VTT process development unit (PDU) uses circulating fluidized bed technology.

European Union (EU)<sup>14–16</sup> (the European Commission and IEA Bioenergy sponsored Pyrolysis Network, PyNe; EU sponsored ThermalNet). VTT was participating in these from their onset.

VTT was the first organization to report fast pyrolysis bio-oil (FPBO) combustion engine tests in a laboratory-scale diesel engine.<sup>17</sup> The aim was to decouple power production from solid biomass fuels to enable intermittent power production from renewables. This was also the emphasis of the first major industrial development, in which VTT participated in relation to fast pyrolysis. Designed by Sipilä and Dr. Kari Saviharju (VTT) and supported by the Finnish and Canadian governments, VTT, Wärtsilä, and Ensyn attempted to develop a concept based on a VTT integration invention and Ensyn pyrolysis technology.<sup>18,73</sup> This collaboration did not meet the goals intended. However, it led VTT to consider the analytics of these biomass-derived liquids<sup>19</sup> from the industrial perspective. From this onward, standardization of products was understood to be a key to successful industrial development. In this area, VTT has been continuously working and developing methods for FPBO characterization<sup>20,21</sup> lead by Dr. Anja Oasmaa, thus building these critical tools for larger scale operations.

Steady-state modeling using AspenPlus for synfuel concepts was already initiated in the 1980s. Models for fast pyrolysis were also built in the 1990s,<sup>22</sup> which were later further developed and used to study advanced concepts designed at VTT.<sup>23,24</sup> Computational fluid dynamic (CFD) modeling of pyrolysis processes, following modeling of combustion and gasification, was initiated at VTT around 2010. Today, CFD modeling is an important tool for the scale-up of these technologies.

While the production technology from wood feedstock has now been demonstrated, upgrading of the product liquid has not been proven beyond laboratory scale. Production of higher value fuels and chemicals remains as the next challenge to improve the competitiveness of fast pyrolysis. The most advanced upgrading method is the hydrotreatment of FPBO, as presented by Dr. Elliott at the Pacific Northwest National Laboratory (PNNL).<sup>25</sup>

One of the alternatives to improve the quality of products is catalytic pyrolysis.<sup>26</sup> VTT was the first to publish results from pilot-scale catalytic pyrolysis of biomass. A 4 day continuous operation has been reported,<sup>27</sup> highlighting the main challenges of this approach: deactivation of the catalyst employed and low yields of the higher value, low oxygen content product. VTT has also collaborated with PNNL and Prof. Abglevor at Utah State

University (USU) in developing lower cost alternative catalysts for catalytic pyrolysis.<sup>28</sup>

Over the years many types of feed materials have been processed at VTT. Most of them have been woody materials (forest residues,<sup>29–32</sup> sawdust, stumps, bark, and lignin<sup>33</sup>), but also waste<sup>34</sup> and fossil materials have been included (initially peat<sup>35,36</sup> and later shale oil). The current emphasis has shifted to waste materials, notably plastic.<sup>37</sup> We expect that the next major industrial efforts will be related to plastics.

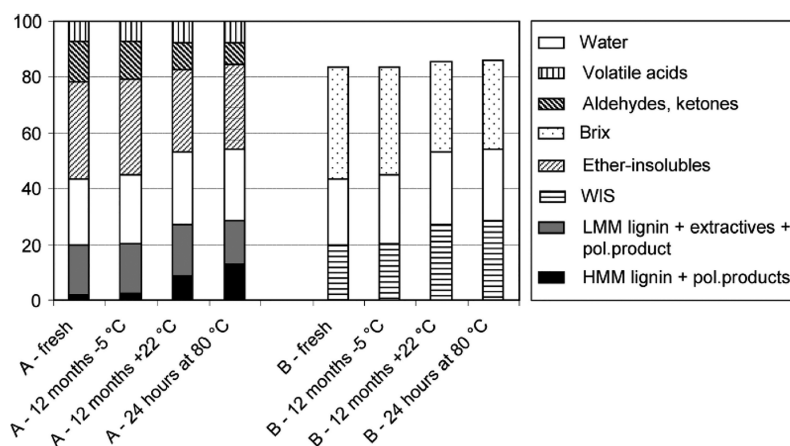
In this paper, the main contributions of VTT to fast pyrolysis bio-oil technology and its commercialization are summarized, from fast pyrolysis technology to the pyrolysis product, its upgrading and standardization, to the methods used for development of fast pyrolysis processes. Although the focus is on the research at VTT, also parallel development elsewhere is shortly mentioned. Also, a vision for future developments is included.

## FAST PYROLYSIS BIO-OIL PRODUCTION

Fast pyrolysis is a high-temperature process ( $\sim 500$  °C), in which biomass is rapidly ( $< 2$  s) heated in the absence of oxygen. A comprehensive description of pyrolysis technologies has been provided by Bridgwater.<sup>38</sup>

VTT has participated in a number of EU projects on the development of fast pyrolysis technologies starting from the 1990s. These included partners from all of the pilot units at the time in Europe: those of ENEL (Italy),<sup>39</sup> Union Fenosa (Spain),<sup>40</sup> and Fortum (Finland).<sup>41</sup> The ENEL plant was based on Ensyn rapid thermal pyrolysis (RTP) technology. There were numerous technical problems with the facility, and it was never operated as designed. Union Fenosa had a fluidized bed technology based on the design of Prof. Scott's group. While Union Fenosa was rather successful in their piloting operations, the low price of mineral oil products eventually ceased interest with these plants. However, experiences in analyzing and treating these difficult liquids at VTT greatly supported later development works. Fortum's technology was their own fluid bed technology. A special advantageous feature in this plant was the bio-oil storage containers. Those containers enabled the separation of extractive-rich top layer from the produced bio-oil. As a result, the solid content of bio-oil was very low.

While the other first industrial operators were looking for replacing heavy fuel oil (HFO) or coal with FPBO, the aim of Fortum was to replace light fuel oil (LFO). Although the value of



**Figure 2.** Composition of pyrolysis liquid based on the solvent extraction scheme. Chemical characterization by measuring sugars by (A) solvent extraction as EISs and (B) Brix method. This figure was reproduced with permission from ref 53. Copyright 2008 American Chemical Society.

LFO was considerably higher than that of coal or HFO, with benefits for renewable fuel thus potentially higher, the low price of mineral oil made Fortum cease development in early 2000.

Up to now, the most important industrial effort, in which VTT has participated in relation to fast pyrolysis, is the development projects of Valmet (Dr. Kari Kuukkanen), Fortum (Jukka Heiskanen), and initially also UPM (Dr. Markku Karlsson). The collaboration was started on the basis of the VTT patented integrated pyrolysis technology.<sup>42</sup> The scale-up to pilot scale was demonstrated at the Valmet facilities, and a pre-commercial, world's largest (30 MW<sub>th</sub>, 50 000 t/a FPBO) biomass fast pyrolysis plant up to now was built for Fortum in the city of Joensuu, Finland (plant is now owned by Savon Voima).

The second largest fast pyrolysis plant (15 MW<sub>th</sub> FPBO) by BTG-BTL/EMPYRO (nowadays owned by Twence) was established in Hengelo (2015), Netherlands (BTG was the technology provider).<sup>43</sup> The principal difference in these demonstration production plants is the reactor type employed: the Fortum unit is using a fluidized bed reactor, whereas the Empyro plant is based on mechanical mixing by a rotating cone. In Renfrew (Canada), Ensyn<sup>44</sup> is operating a plant with a biomass input capacity of 3.5 t/h (about 8 MW<sub>th</sub> FPBO). Ensyn and Envergent are constructing a new plant to Côte Nord with a design capacity of 30 MW<sub>th</sub> FPBO. Two large-scale pyrolysis units using BTG-BTL technology are under construction in Europe: one in Finland (GFN, Lieska) aiming to replace gas oil and the other in Sweden (Pyrocell, Gävle) to produce FPBO to co-feed with vacuum gas oil (VGO) in an existing oil refinery of Preem. The combined Canadian–European FPBO production capacity will exceed 180 000 tonnes in 2021.

## LEARNINGS FROM PROCESS DEVELOPMENT

VTT's pilot unit uses a circulating fluidized bed reactor technology (Figure 1) concept originally designed and reported by the IEA group<sup>6</sup> and later developed further among others by Ensyn. Circulating fluidized bed reactor technology offers among others a good heat transfer environment as a result of the large amount of hot circulating solid particles; it is efficient at ash removal as a result of an efficient cyclone setup; and most importantly, circulating fluidized beds are scalable to industrial scale. On the other hand, circulating fluidized bed units have higher electricity consumption, and a higher amount of circulated gas makes the liquid recovery unit larger compared to other fast pyrolysis reactor types.

Over the years, several process developments were made to the reactor, recovery, and gas circulation units. For example, VTT found the use of a so-called liquid ring compressor<sup>45</sup> to be very effective for recirculating non-condensable gases compared to traditional pumps compressors that are more prone to tar-induced fouling. However, probably the most important discovery was the concept of process integration to a fluidized bed boiler.<sup>46,47</sup> This so-called integrated concept enabled savings in investment costs as well as provided more energy efficient utilization of char and non-condensable gases in the fluidized bed boiler unit.<sup>23,24</sup> The integrated concept is very well-suited, for example, for pulp and paper mills because those very commonly have large fluidized bed power plants to produce the steam and electricity needed for pulp and paper production.<sup>24,48–50</sup>

Successful industrial demonstration of the integrated fast pyrolysis concept was performed at the Fortum Joensuu plant.<sup>51,52</sup> During the scale-up and demonstration projects, we learned that the integration of combustion and pyrolysis processes also needs to be designed carefully. One thing to consider was the particle size of sand. In the case of Joensuu, the particle size of the sand in the power plant was larger than the particle size typically used in fast pyrolysis, which, in turn, affected the design of the fast pyrolysis reactor. Furthermore, also the location in the boiler where sand input for fast pyrolysis was taken from affected the design of the fast pyrolysis reactor. In the case of Joensuu, the power plant was based on the bubbling fluidized bed process that operates typically around 800 °C, which is significantly higher than the typical operation temperature of fast pyrolysis. In addition to the high temperature of sand, the possible intake of unburned char particles also needed to be taken into account in the design of the fast pyrolysis process. One important lesson learned was also that introducing hot sand to the fast pyrolysis reactor after fluidizing gas and biomass feedstock (contrary to the Ensyn concept) improved the practical operation of the reactor as a result of more simple feeding of biomass into the reactor.

## CHEMICAL COMPOSITION AND BEHAVIOR OF FPBO

FPBO is a mixture of many components and not uniquely defined. IEA Bioenergy Task 34 on pyrolysis suggested the following definition for fast pyrolysis bio-oil: "Bio oil is a complex mixture of, for the most part; oxygenated hydrocarbon

Table 1. Composition of Pyrolysis Liquid Based on the Solvent Extraction Scheme and GC/MS<sup>a</sup>

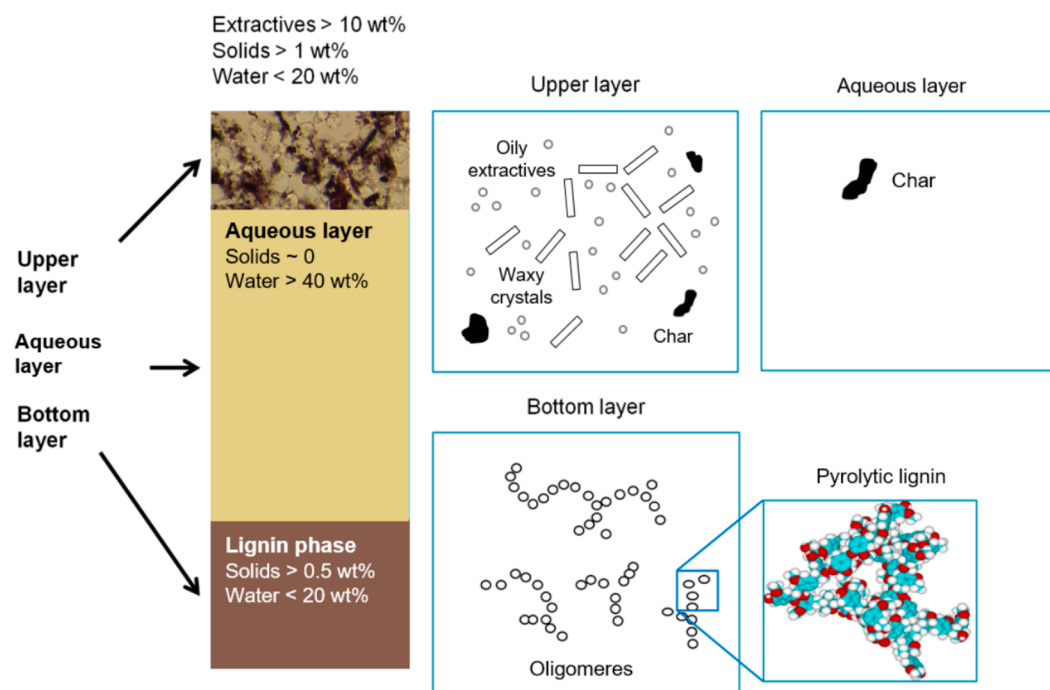
fast pyrolysis bio-oil	pine		forest residue			
	bottom 97%		bottom 89%		top 11%	
	wet wt %	dry wt %	wet wt %	dry wt %	wet wt %	dry wt %
water	23.9	0	24.4	0	19.5	0
acids	4.3	5.6	3.3	4.4	6.4	7.9
formic acid		1.51		1.46		
acetic acid		3.38		7.35		6.01
pioplonic acid		0.20		0.18		0.18
glycolic acid		0.55		0.33		
alcohols	0.23	0.93	0	0	0.16	0.20
methanol		0.63		0		0
ethylene glycol		0.30		0		0.20
aldehydes, ketones, turans, and pyrans	17.4	22.3	20.4	27.0	12.8	15.9
acetaldehyde, hydroxy-		8.93		8.66		8.94
propionaldehyde, 3-hydroxy		0.75		1.17		1.02
hydroxypropanone (acetol)		2.84		2.55		2.25
butanone, 1-hydroxy-2-		0.23		0.22		0.20
butandial or propanal		0.29		0.73		0.64
cydopentene-1-one, 2-hydroxy-2-		0.84		0.21		0.19
cydopentene-3-one, 2-hydroxy/-1-methyl-1-		0.53		0.50		0.41
furanone, 2(5H)-		0.69		0.73		0.65
furaldehyde, 2-		0.54		0.67		0.55
furaldehyde, 5-(hydroxymethyl)-, 2-		1.14		0.44		0.38
pyran-4-ane, 3-hydroxy-5,6-dihydro-, (4H)-		0.72		1.38		1.18
pyran-4-one, 2-hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-		0.39		0.14		0.12
sugar type compounds	34.4	45.3	28.8	38.1	21.9	27.1
anhydro-β-D-arabino-furanose, 1,5-		0.27		0.17		0.12
anhydro-β-D-xylofuranose, 1,5-		0		0.33		0.31
anhydro-β-D-glucopyranose (levoglucosan)		4.01		3.48		3.31
dianhydro-α-D-glucopyranose, 1,4:3,6-		0.17		0.15		0.14
cellobiosan		1.3		NA		NA
cellotriosan		0.1		NA		NA
LMM lignin	13.4	17.7	12.0	15.8	15.5	19.2
catechols		0.06		0.09		0.08
lignin-derived phenols		0.09		0.22		0.19
guaiaicol		0.52		0.28		0.25
guaiaicol, 4-methyl-		0.49		0.15		0.14
guaiaicol, 4-propenyl-(trans) (isoeugenol)		0.40		0.12		0.13
vanillin		0.50		0.23		0.21
homovanillin (phenylacetaldehyde, 4-hydroxy-3-methoxy-)		0.27		0.09		0.09
acetoguaiaicol (phenylethanone, 4-hydroxy-3-methoxy-)		0.22		0.09		0.08
coniferylaldehyde		0.26		0.05		0.04
syringol		0		0.40		0.36
syringol, 4-methyl-		0		0.29		0.26
syringol, 4-allyl-		0		0.28		0.06
syringol, 4-(1-propenyl)-, trans		0		0.28		0.27
syringaldehyde		0		0.41		0.37
sinapaldehyde (trans)		0		0.57		0.54
HMM lignin	1.95	2.6	4.3	5.6	7.6	9.5
extractives	4.35	5.7	2.8	3.7	16.4	20.4
solids	0.011	0.014	0.040	0.053	2.90	3.60

<sup>a</sup>The table combines the information on the same FPBO samples using both the solvent fractionation scheme at VTT and GC/MS at TI (Dr. Meier). This table was reproduced with permission from ref 54. Copyright 2015 American Chemical Society.

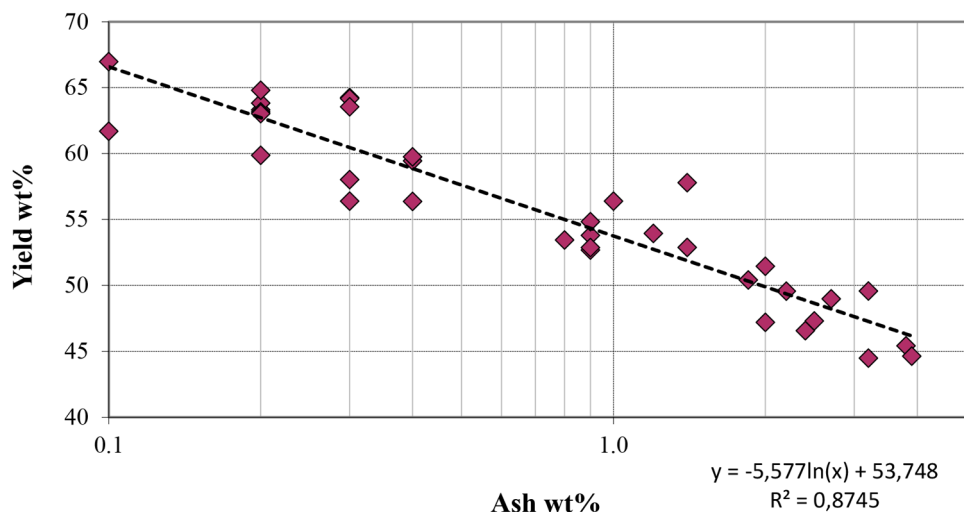
fragments derived from the biopolymer structures. It typically contains 15–30 wt % water. Common organic components include acetic acid, methanol, aldehydes and ketones, cyclopentenones, furans, alkyl-phenols, alkylmethoxy-phenols, anhydrosugars, and oligomeric sugars and water-insoluble lignin-derived compounds. Nitrogen- and sulfur-containing com-

pounds are also sometimes found depending on the biomass source.” FPBO is registered with the Chemical Abstracts Service (CAS) as CAS Registry Number 1207435-39-9.

VTT has focused on developing rapid methods to follow the changes in compound groups. The solvent-based fractionation scheme<sup>30,53</sup> has been widely used in comparison of various



**Figure 3.** Schematic representation of the multiphase structure of fresh FPBOs. The upper layer is the extractive-rich layer. The aqueous phase separates out as a result of high moisture or ash content of the feedstock or aging. Micelles are lignin-derived water-insoluble substances in the bottom layer. This figure was reproduced with permission from ref 55. Copyright 2016 American Chemical Society.



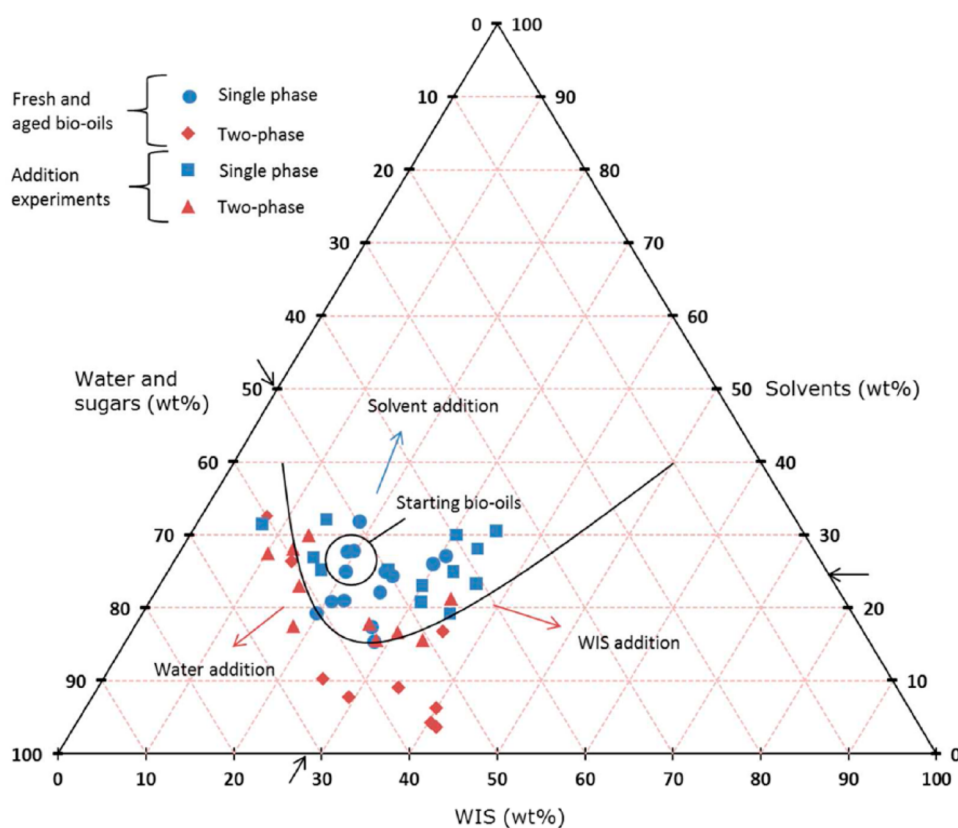
**Figure 4.** Correlation of the organic yield with the ash content of wood feedstocks (bark-free soft and hard woods and forest residues). This figure was reproduced with permission from ref 56. Copyright 2010 American Chemical Society.

FPBOs and following the changes during storage and upgrading (Figure 2). Table 1 shows the chemical composition of pine and forest residue FPBOs (having a separate extractive-rich top phase), combining the information on both the solvent fractionation scheme by VTT and gas chromatography/mass spectrometry (GC/MS) by Thünen Institute (TI, former IWC, Germany, Dr. Meier).

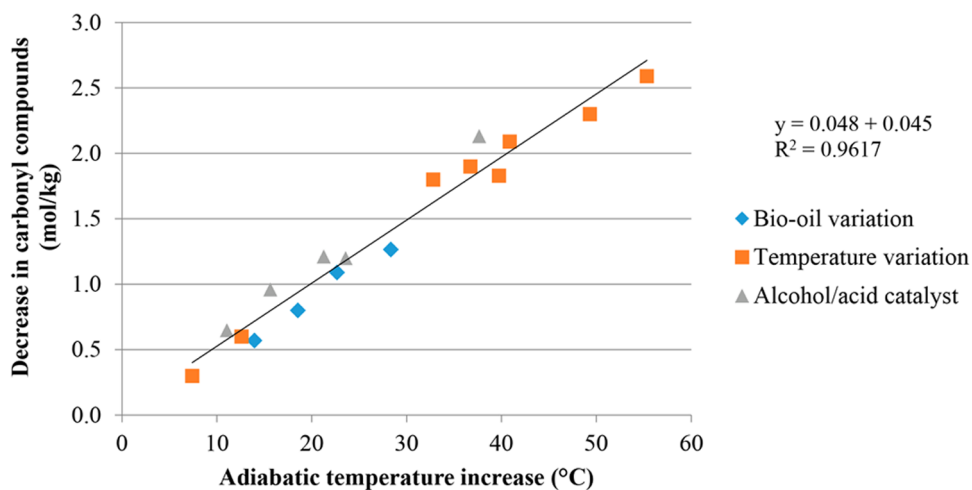
**Multiphase Structure of FPBOs.** FPBOs are typically visually homogeneous single-phase liquids. However, they possess a multiphase structure, which has to be observed when handling and storing the bio-oil. They can separate into various phases mainly as a result of the following reasons:<sup>55</sup> (i) feedstocks, like forest residues or bark, contain a lot of neutral

extractives, which have very limited solubility in polar FPBO; (ii) feedstock is too moist for pyrolysis, which increases the total water content of FPBO; (iii) feedstock contains a high amount of ash and alkali metals, which increases the water content and reduces the organic content of produced liquid; and (iv) FPBO aging, which yields to increase high-molecular-weight material. Also, solid char particles form a separate phase inside FPBO, which has to be notified. Figure 3 schematically presents the multiphase structure of the fresh phase-separated bio-oil from forest residues.

The bio-oil yield from wood materials has been shown to correlate with the feedstock ash content (Figure 4).<sup>56,57</sup> Especially, potassium has been shown to catalyze decomposition



**Figure 5.** Ternary-phase diagram of phase stability, including addition experiments with water, a water-insoluble (WIS) fraction, and a model solvent mixture. This figure was reproduced with permission from ref 54. Copyright 2015 American Chemical Society.



**Figure 6.** Correlation between the increase in the adiabatic temperature ( $^{\circ}\text{C}$ ) and the decrease in carbonyl compounds ( $\text{mol}/\text{kg}$ ) under varying aging conditions. The displayed trendline and correlation coefficient are for a linear regression model containing all data points. This figure was reproduced with permission from ref 70. Copyright 2016 American Chemical Society.

of liquid compounds and increase gas, char, and reaction water yields.<sup>58</sup> The last one is mainly due to the fact that ash and more specifically alkali metals catalyze pyrolysis reactions, yielding lower organic and higher char yields.

The rest of the ash can be removed, for example, by subsequent hot-vapor filtration (HVF)<sup>59–61</sup> or ion exchange,<sup>62,63</sup> although both of those are still at the development scale. In industrial scale, the major challenges of HVF include how to keep the filter open for a longer operational time. VTT has patented<sup>64</sup> and is developing a new type of filter system,

where the pressure drop across the filter in bench scale was stable during an operation period of 8 h. The development work is ongoing.

As a result of the high amount of reactive oxygen-containing species FPBOs changing by the temperature and time, they age.<sup>65</sup> The National Renewable Energy Laboratory (NREL, the U.S.A.) and VTT developed in cooperation the test method to follow aging of FPBO.<sup>66–68</sup> In aging, the amount of water-insoluble material increases (polymerization and condensation reactions) and the amount of “solvents” (aldehydes, ketones,

and alcohols) decreases, which results in separation of a water-insoluble fraction containing lignin-derived material and polymerization/condensation products. Figure 5 shows a recent phase diagram for FPBOs.<sup>54</sup> This diagram has more recently been developed further by Li et al.<sup>69</sup> Aging of FPBOs can be diminished by storage in cold, the addition of alcohols, diminishing the amount of ash/alkali metals in the bio-oil, or stabilization.<sup>65–67</sup>

**Controlling the Phase Separation.** Phase separation can be controlled by following the change in the chemical composition. An increase in the relative amount of the polar (water and “sugars”) fraction above 60 wt % or water-insoluble (WIS, lignin-derived material, extractives, solids, and polymerization products) fraction above 35 wt % (increase in polymerization products) or a decrease in the amount of co-solvents (light aliphatic and aromatic acids, aldehydes, ketones, alcohols, and monophenols) to below 15 wt % (reactions of carbonyl compounds leading to WIS material) may lead to phase separation. Phase separation can be prevented by the choice of the feedstock, pretreatment of the feedstock by alkali removal, controlling the moisture contents of the feedstocks, or storing the FPBO in the cold and for a short period before use.

Aging reactions also cause heat generation, which has to be notified especially when planning commercial-scale storage. There is a clear correlation of the increase in the adiabatic temperature of FPBO to the decrease in carbonyl compounds of FPBO as a result of aging (Figure 6)<sup>70</sup> for various bio-oils, using various temperatures, alcohol additions, or acid catalysts.

## ■ APPLICATIONS

During the early years of research, the application development for FPBOs at VTT was focused on the engine use.<sup>17</sup> Industrial development was the aim for VTT from the start. Further industrial development was performed in cooperation with Wärtsilä.<sup>18</sup> It was concluded that, to proceed further with slow-speed diesel engines, the fuel oil quality of FPBO should be improved, especially related to its acidity, stability, and solid content.<sup>71,72</sup>

During around 2000, VTT worked in cooperation with Fortum (nowadays Neste) at their fast pyrolysis pilot plant in Kilpilahti, Finland. Their focus was on light fuel oil use. Heavy fuel oil replacement in burner applications<sup>74–76</sup> started in 2007 when the consortium of Fortum, Valmet, and UPM decided to build the world's first integrated fast pyrolysis plant. The produced FPBO was used in small-scale district heating plants. This overall concept has been successfully demonstrated to be viable at commercial scale by Fortum.<sup>77</sup>

Lately, VTT has actively been doing research on other FPBO applications, such as refinery feed and upgrading to transportation fuels and chemicals. Good reviews on these topics are provided, for example, by Zacher et al.,<sup>78</sup> Zhang et al.,<sup>79</sup> and Stankovikj et al.<sup>80</sup>

## ■ UPGRADING

Considering fuel oil applications, FPBOs possess some detrimental behaviors, most of which have to be notified and controlled. These include solids, ash, alkali metal, and Si contents, acidity, polarity, inhomogeneity, high water content, instability, and heat formation. At VTT, the quality improvement of FPBO has been focused on physical treatments, like removing light volatiles with acids,<sup>81,82</sup> solvent addition,<sup>32</sup> fractionation,<sup>83</sup> and hot-vapor filtration, or on chemical

modification, like esterification,<sup>84</sup> catalytic pyrolysis,<sup>85–87</sup> and co-processing.<sup>88</sup> The main findings were as follows: (i) Hot condensation (condensing temperature around 40 °C) is a cost-effective method to decrease the final water content of FPBO. Simultaneously, a part of acids and light aldehydes, which contribute to the instability of FPBO, can be removed.<sup>81–83</sup> (ii) The addition of alcohols dilute the FPBO and improve its storage stability.<sup>22,32,83</sup> (iii) Hot-vapor filtration is effective in removing metals from pyrolysis vapors.<sup>89,90</sup> This is beneficial for further hydrodeoxygenation (HDO), contributing to a longer lifetime of catalysts. However, it also decreases the organic yields. Also, long-duration tests still have to be proven. (iv) Esterification and azeotropic water removal can improve the unfavorable properties that restrict the use of FPBO in many applications. Among the main issues are high acidity, instability, and water and oxygen contents, which give rise to corrosiveness, polymerization during storage, and a low heating value. However, the disadvantages include economics and a high alcohol content of the product liquid. (v) Evaluation of the catalyst in pyrolysis tests showed that the presence of biomass metals on the catalyst altered the functionality of the catalyst, likely by introduction of some basic sites, which led to the deterioration of its catalytic performance.<sup>85–87</sup> (vi) Co-processing of bio-oil in refinery fluid catalytic cracking (FCC) would have many economic advantages compared to other upgrading technologies because no essential modifications to the refinery are needed. However, because of its different chemical compositions, the introduction of bio-oil into the FCC unit will introduce uncertainty to the refinery operation.<sup>88</sup>

VTT has only recently focused on the HDO of FPBOs. A comprehensive review on this topic has been provided by Elliott.<sup>91</sup> The VTT characterization scheme has been used in evaluating the composition of HDO products.<sup>92</sup>

## ■ NORMS AND STANDARDS

Products from FPBO are entering into the market to replace natural gas and heating oil or to be used in co-refining for higher value fuels. Standardized fuels are essential to allow for successful market implementation. To proceed with standardization, commercial opportunities must be defined. Therefore, adequate amounts of liquid fuels should be available; long-duration application experiments with published data should be carried out; and accurate analytical test methods should be validated.

VTT has provided guidelines<sup>93</sup> and developed test and rapid characterization methods for FPBO since the 1990s.<sup>94–97</sup> The test methods have been validated by several IEA round robins.<sup>98–102</sup> Cooperation has been performed especially within the IEA Pyrolysis Networks.<sup>103–105</sup> These analytical test methods form the basis of present FPBO standards.

VTT initiated the discussions about standardization of fast pyrolysis bio-oil as a fuel with the European Committee for Standardization (CEN) in early 2000.<sup>106</sup> In 2007, a pyrolysis oil standard initiative for ASTM was initiated, which led to a burner fuel standard ASTM D7544:2017. VTT worked as an advisor, especially concerning the test methods needed. As a result of this cooperation, the solid content method developed at VTT obtained the standard ASTM D7579.<sup>106</sup> In Europe, a WG149 (led by SFS Finland and VTT) was set up to proceed with the mandate M525 for fast pyrolysis oil, which allowed for the process to proceed toward: (a) a European standard for a quality specification for pyrolysis oil replacing heavy fuel oil in boilers, (b) a European standard for a quality specification for



pyrolysis oil replacing light fuel oil in boilers, (c) a technical specification for a quality specification for pyrolysis oil replacing fuel oils in stationary internal combustion engines, (d) a technical specification for a quality specification for pyrolysis oil suitable for gasification feedstock for production of syngas and synthetic biofuels, and (e) a technical specification for a quality specification for pyrolysis oil suitable for mineral oil refinery co-processing. The European standard for the use of FPBO in large-scale industrial boilers ( $\geq 1 \text{ MW}_{\text{th}}$ ) was obtained in 2017 (EN 16900:2017).<sup>107</sup>

There are not yet other standards for FPBO. A Technical Report (EN/TS 17103:2017) was published for the use of FPBO in internal combustion engines (both compression ignition and gas turbines). More data are needed on the properties of FPBO for stationary internal combustion engine (ICE) use and to determine combustion properties before proceeding toward the standard. Also, long-duration tests in ICE need to be carried out. In the European project “Residue2Heat” (2016–2019), lacking information was created to enable standardization of FPBO in small-scale residential boilers. A discussion paper on FPBO used in small-scale boilers ( $\leq 200 \text{ kW}$ ) has been published. Standards for co-refining are under work in the EU 4Refinery project.<sup>108</sup>

VTT has also been active in obtaining data for Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) registration of FPBO. In the EU, registration to the European Chemical Agency (ECHA) must be made if FPBO is produced or imported to the EU.<sup>107</sup>

### ■ TECHNO-ECONOMIC ASSESSMENT (TEA)

Techno-economic assessments are standard tools for evaluating and comparing technologies and processes. A TEA has two major types of input: performance balances and capital costs. Accurate mass and energy balances may be derived when adequate large-scale experimental data for industrial-scale operation is available for performance simulation. An accurate investment estimate is possible when data based on similar process unit costs are available.

Although TEAs are important in process evaluation during the R&D stage, neither of the above input is generally available. Thus, the uncertainty in early TEAs is always large. The role and resources of TEA needs to be clearly weighted and established to be able to produce valuable information.

The larger the scale operational data are available for the estimate, the more accurate TEA results may be generated. It is also self-evident that the amount of resources invested in a TEA has a considerable effect for the quality of the results.

Early successful examples of TEAs in which VTT participated were the IEA Bioenergy liquefaction assessments,<sup>6,7</sup> suggesting that fast pyrolysis would be preferable to high-pressure liquefaction (which nowadays is called hydrothermal liquefaction). These assessments paved the way for many countries emphasizing fast pyrolysis in public research funding over the next 20 years.

The IEA studies also addressed the two big challenges related to TEAs: the small scale of experimental performance data at the time available to derive industrial-scale plant performance and estimation of investment costs based on the performances with considerable uncertainty.

TEAs have always been an integral part of publicly funded projects. Unfortunately, the objectives for these studies have often been too ambitious compared to the resources available. Early VTT studies comparing biomass conversion to heat,

power, and biofuels are no exception to this.<sup>73</sup> VTT has been employing the AspenPlus simulation tool for assessing industrial plant performance for the processes since the 1980s.

The RAND Corporation published several reports analyzing this dilemma in the 1970s<sup>109,110</sup> for the U.S. DOE. One of the main conclusions was that predicted mass and energy balances for plants should be emphasized over capital cost estimates when assessing a technology with a low level of development. The RAND reports also highlighted the fact that capital cost estimates may be much more off than traditionally assumed when new technologies are evaluated.

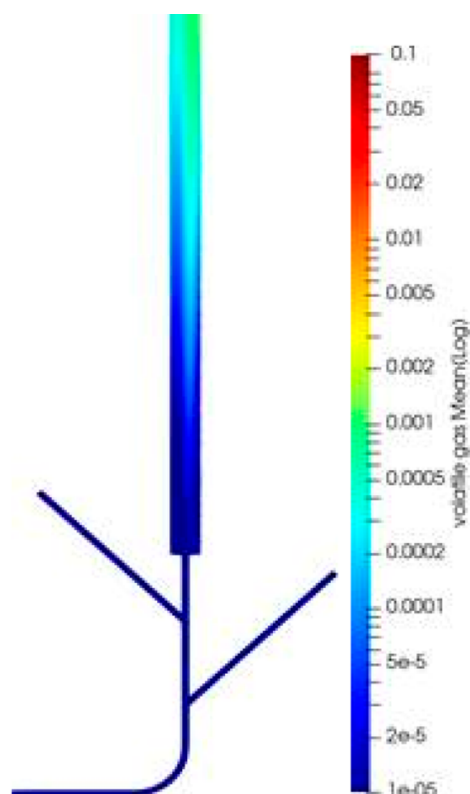
Life cycle analysis (LCA) have also been carried out at VTT related to fast pyrolysis.<sup>111</sup> Renewable Energy Directive (RED) methodology for calculating the greenhouse gas emissions of biofuels and bioliquids was employed. Substituting heavy fuel oil with pyrolysis oil in heat production probably reduces greenhouse gas emissions. However, the methodology does not state accurately enough how to define the system boundary or how to allocate emissions in a case situation with several products.

### ■ CFD MODELING SUPPORT FOR PYROLYSIS PROCESS DESIGN

Designing a pyrolysis unit relies on information on the conversion rates and heat and mass transfer phenomena that take place in the process. All process scales from laboratory to full industrial scale benefit from evaluation of process behavior prior to construction of the unit, so that modifications to the design can be easily performed to optimize process output. The easiest method to account for all of the coupled phenomena is three-dimensional (3D) CFD modeling that predicts concentrations of gas components and solid particles (fuel, bed particles, catalyst, etc.), gas and solid velocities, and temperatures of the phases in the 3D reactor volume. CFD modeling is used at VTT to optimize process designs and produce data on residence times of the fuel and different chemical components in different conditions in the process, which is important for prediction of the conversion processes and rates. CFD modeling is also used at VTT to help to interpret measurement results from laboratory and pilot scale and to scale up the results to industrial scale. For some fuels, kinetic mechanisms and data are available from the literature,<sup>112,113</sup> but in many cases, kinetic data need to be determined from pyrolysis tests.

Accurate modeling of the flow patterns in a fluidized bed as a function of time is feasible with the two-fluid Eulerian–Eulerian continuum approach that uses the kinetic theory description of granular flow.<sup>114</sup> An example of a transient simulation of a laboratory-scale fluidized bed pyrolysis unit is shown in Figure 7, in which the concentration of pyrolysis gases in the critical bottom part of a laboratory unit are shown. The purpose of the simulation was to evaluate different feeding locations and geometry designs, of which the figure shows the final design. The simulations were carried out with OpenFOAM software using the kinetic theory of granular flow approach. In this design simulation, the net pyrolysis rate was described by a simple empirical correlation that takes the particle size and temperature into account.

The characteristics of fluidized bed pyrolysis complicate CFD modeling of industrial-scale units as a result of the combination of a large process size, the multiphase nature of the flow, and characteristic small flow structures that are a result of clustering of solid particles. Accurate modeling requires a fine mesh resolution, which can be difficult to achieve in the case of



**Figure 7.** Concentration of pyrolysis gases in a lab-scale fluidized bed pyrolysis unit. Fuel is fed from the right, with hot bed material from the left and air from below. VTT data were used.

industrial size processes as a result of the required very long simulation times. Thus, alternative approaches for faster but more approximative modeling of fluidized beds have been introduced. At VTT, a fast method for simulation of industrial fluidized bed processes has been developed by Taivassalo et al.,<sup>115</sup> whose approach is based on time-averaged transport equations and modeling of the steady-state conditions, thus avoiding integration over process time. This method has been successfully used for solving design and emission problems in circulating fluidized bed (CFB) combustors. The method has been extended to pyrolysis by including detailed pyrolysis reaction mechanisms taken from the literature. It has been used for evaluation of design alternatives for industrial fluidized bed pyrolysis units.

## ■ VERDICT

VTT overall is a major recipient of public research and innovation funding in the EU. The research done at VTT has largely been funded by public national and European funding agents. Therefore, the following is dedicated for evaluating pros and cons of the public funding systems encountered over the years. To begin with, international collaboration is a must to keep up the required communication with other relevant operators in the field.

The role of an enthusiastic public servant responsible for allocating funding cannot be emphasized too much. However, the larger the funding agent, the less room there is for innovative management, which is a key factor in any success. An example for the successful management is the IEA collaboration nourished by Overend and Stevens in the 1980s.<sup>3–8</sup> Large organizations build bureaucratic decision-making procedures

for obvious reasons such as impartiality, transparency, and control of public funds. However, this tends to produce mediocrity as a result of the need for detailed advanced planning with reduced and cumbersome possibilities for changes in living projects. Many public projects fail their recorded, often vague, yet necessarily ambitious objectives to reach the sometimes unrealistic requirements by public funding agents. Additionally, a single project or even a program is rarely enough to bring technology to an industrially sufficient risk level. Therefore, success may be an elusive goal, because true results may only appear long afterward. Public projects therefore serve principally as a training ground for industrial projects. However, they have a critical role in building networks, expertise, and knowledge for focused industrial projects.

The industrial demonstration projects are therefore the true measurement for the qualifications of an applied R&D organization, like VTT. A key collaboration for VTT in pyrolysis has been the work with Valmet, which started around 2008. Toward the end of 2013, an industrial-scale demonstration plant was in commission integrated to a Fortum combined heat and power (CHP) boiler. We consider this as a rapid and successful scale-up and report below one important reason for a cost-effective operation.

The series of RAND reports<sup>109,110</sup> analyzed the U.S. DOE funded process development related to an intended synfuel industry (1970s and early 1980s). Overall, the most important connecting factor in common to success was the ability to transfer as much as possible knowledge when the responsibility of development is changed from one organization to another. In the Valmet collaboration, VTT made a directed effort in reporting all of its experiences under our control to Valmet. It was initially critically important to also report the past mistakes, because Valmet was operating at a pilot scale with much higher expenses than VTT earlier. The VTT policy was geared to help in reducing development costs.

Resources required for pyrolysis R&D are typically expensive: (i) an experienced and innovative project management is required; (ii) a critical mass of people with several years of experience is required in experimental R&D, modeling, and chemical and process analysis; (iii) an industrially functional CFD code for pyrolysis is possible only with an experienced team and well-developed models; and (iv) a pyrolysis pilot typically costs 1–3 million € in 2020.

Process development is necessarily a long-term venture requiring experimental work in several scales ranging from low-cost bench work all of the way to higher cost pilot operation. This route requires the abovementioned resources. However, not only are expensive resources needed, but luck and perseverance are also factors in success.

## ■ CHALLENGES AND FUTURE RESEARCH DIRECTIONS

When looking back at VTT efforts in fast pyrolysis, the following issues were critical for successful development work: an industrially relevant target and understanding the need for norms and standards, steady funding, close cooperation with industry, good teamwork, adequate resources, national and international networks, and active publishing policy.

The fast pyrolysis production technology for wood has been demonstrated and commercialized for replacing natural gas and heating oil. In this context, feedstock purchase and product applications with logistics should be very well-planned. Also, large storage containers and long-duration storage of FPBO

should be avoided as a result of the instability of the FPBO. Preferably, the FPBO should be used close to the production site, having a minimal storage time. Production of higher value fuels and chemicals remains as the next challenge to improve the competitiveness of fast pyrolysis. One of the alternatives is catalytic pyrolysis. A lot of present research is focusing on co-refining options and advanced biofuels for marine and jet fuels. Standards are already available for industrial boiler use, and work is going on to cover other applications as well. Upgrading of the FPBO has not yet been proven beyond laboratory scale. The challenges here and also in catalytic pyrolysis include to remove alkali and other catalyst poisons or develop cheap replaceable or regenerable catalysts with a long lifetime. Also, cheaper hydrogen sources are needed. Process integrations should be used where possible.

In addition to climate change perspectives, also the biodiversity and ecological points of views direct our research to take sustainability, carbon footprint, and material and energy efficiencies more into account. Even the role and concept of sustainable biomass is currently being debated in the global community. These boundary conditions have led us to pursue other feedstocks than wood. Additionally, we have understood that certain fast pyrolysis reactor configurations are more suitable than others for different purposes, when considering both feedstock and end-use applications.

In Europe, REDII defines the biomass residues and wastes to be used. For pyrolysis of biomass, the feedstock base will move toward wood waste, like used wood, cardboards, and wood packages, side products, like black liquor/kraft lignin, and bark, as well as agro and residual biomasses, which cannot be used for food or fodder. Also, feedstocks that create environmental problems, like water hyacinth or various manures, are also options for energy production. These new lower quality feedstocks create new process challenges related, i.e., to ash components, extractives, nitrogen, chlorine, sulfur, phosphorus, and toxic compounds. Also, seasonal variations have to be covered, and mixed feeds have to be considered. It is evident that the present processes have to be improved. Modeling, tightly coupled to laboratory- and pilot-scale studies, will play an increasingly large role in process development and equipment design.

Biomass co-pyrolysis with other feedstocks is an interesting option, which is claimed not only to enhance physicochemical properties of pyrolysis products but also to effectively realize recycling of wastes.<sup>116</sup>

A circular economy is currently dictating the use of waste materials. Mechanical recycling of plastics does not fulfill the recycling targets, and it is obvious that also chemical recycling, like pyrolysis, is needed.<sup>37</sup> However, legislative aspects have to be clarified, and pyrolysis should be included as one chemical recycling method. We expect that the next major industrial efforts in pyrolysis will be related to plastics. The pyrolysis product composition depends largely upon the feedstocks. High yields of monomers can be obtained from feedstocks, like polystyrene, and from mixed polyethylene- and polypropylene-containing plastic waste, the product might be, i.e., diesel fuel. Here, the reactor technology plays an important role. Simple, robust, modular, easily scalable reactor types that can handle dirty heterogeneous feed and quality variations are needed. For example, VTT has taken an effort to develop modularly designed extruder reactors where sample pretreatment, pyrolysis, and post-treatment will be handled basically in the same unit.<sup>117</sup>

Proof of concept has been carried out by a client, and the next step is piloting.

As a summary, in our opinion, the role of fast pyrolysis in the larger scheme of things has changed from being a technology for producing liquid fuels to being an efficient process engine for a circular economy. For example, recycling of plastics, removal of contaminants, and recovery of nutrients from waste streams are very interesting opportunities that the fast pyrolysis community should focus on more because the potential is great but yet still untapped.

## ■ AUTHOR INFORMATION

### Corresponding Author

Anja Oasmaa – VTT Technical Research Centre of Finland, Limited, FI-02044 Espoo, Finland; [orcid.org/0000-0003-4524-8002](https://orcid.org/0000-0003-4524-8002); Email: [anja.oasmaa@vtt.fi](mailto:anja.oasmaa@vtt.fi)

### Authors

Jani Lehto – VTT Technical Research Centre of Finland, Limited, FI-02044 Espoo, Finland

Yrjö Solantausta – VTT Technical Research Centre of Finland, Limited, FI-02044 Espoo, Finland

Sirpa Kallio – VTT Technical Research Centre of Finland, Limited, FI-02044 Espoo, Finland

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.energyfuels.1c00177>

### Notes

The authors declare no competing financial interest.

### Biographies

Anja Oasmaa obtained her Ph.D. and Lic.Sc. (Tech.) degrees from Aalto University and University of Jyväskylä, Finland, respectively, and is a senior principal scientist and principal investigator at VTT Technical Research Centre of Finland, Ltd. She has over 35 years of expertise in thermal conversion processes, especially in pyrolysis, and has a wide global network. She has developed analytical methods, norms, and standards for bio-oils. She is actively involved in circular economy work at VTT and applying pyrolysis technology for plastics.

Jani Lehto obtained his Doctor of Science (Technology) degree from Tampere University of Technology and is the former vice president at VTT Technical Research Centre of Finland, Ltd. During his VTT career, he was in charge of the thermochemical conversion research of VTT, including fast pyrolysis. Prior to VTT, he worked as product manager, Pyrolysis System for Valmet Technologies. Currently, he works for Natural Resources Institute of Finland (LUKE) as vice president.

Yrjö Solantausta obtained his Ph.D. degree from Aston University and is a senior principal scientist at VTT Technical Research Centre of Finland, Ltd. He has 40 years of expertise in thermal conversion processes, especially in pyrolysis. He has published techno-economic assessments of biomass liquefaction processes, and he has lead three IEA networks on the field.

Sirpa Kallio obtained her D.Sc. (Tech.) degree from Aalto University and is a principal scientist and project manager at VTT. She has 32 years of expertise in CFD modeling of multiphase processes. Her main research topic is modeling of thermal conversion in fluidized beds, and she has designed and used pilot units for experimental fluidized bed studies.

## ACKNOWLEDGMENTS

The entire pyrolysis research team at VTT is acknowledged, especially Christian Lindfors, Taina Ohra-aho, Elmeri Pieni-häkkinen, Eeva Kuoppala, and Jaana Korhonen. Antti Arasto and Tom Granström are acknowledged for additional comments. Peyman Davvalo Khongar, Timo Niemi, and Juho Peltola are acknowledged for inputs to the CFD modeling section. Jessica Vepsäläinen and Päivi Vahala-Partanen are acknowledged for formatting.

## REFERENCES

- (1) Garret, D.; Mallan, G. Pyrolysis process for solid wastes. U.S. Patent 4,153,514, May 8, 1979.
- (2) Rust International Corporation. *Final Report. An Investigation of Liquefaction of Wood at the Biomass Liquefaction Facility Albany, Oregon Battelle Pacific Northwest Laboratories Contract B-B2471-A-G and Department of Energy Contract DE AC01-78ET 23032 Wheelabrator Cleanfuel Corporation*; Rust International Corporation: Birmingham, AL, 1982; Technical Report DOE/ET/23032-T1, DOI: 10.2172/12316271.
- (3) Kjellström, B. A study of a biomass liquefaction test facility. *Final Report of IEA Cooperative Project Biomass Liquefaction Test Facility*; Statens Energiverk: Stockholm, Sweden, 1985.
- (4) Beckman, D.; Bergh, A.; Elliott, D. C.; Kannel, A. *IEA Co-operative Project D1, Biomass Liquefaction Test Facility Project, Vol. 2: State-of-the-Art Review*; National Technical Information Service: Springfield, VA, 1988; DOE/NBM-1062.
- (5) Elliott, D. *IEA Co-operative Project D1, Biomass Liquefaction Test Facility Project, Vol. 4: Analysis and Upgrading of Biomass Liquefaction Products*; National Technical Information Service: Springfield, VA, 1988; DOE/NBM-1062.
- (6) McKeough, P.; Nissilä, M.; Solantausta, Y.; Beckman, D.; Östman, A. Techno-economic Assessment of Direct Biomass Liquefaction Processes. *Final Report of IEA Cooperative Project Biomass Liquefaction Test Facility. VTT Research Reports*; VTT: Espoo, Finland, 1985; Vol. 337, pp 139.
- (7) Beckman, D.; Elliott, D. C.; Gevert, B.; Hörnell, C.; Kjellström, B.; Östman, A.; Solantausta, Y.; Tulenheimo, V. Techno-economic Assessment of Selected Biomass Liquefaction Processes. *Final Report of IEA Cooperative Project Direct Biomass Liquefaction. VTT Research Reports*; VTT: Espoo, Finland, 1990; Vol. 697, pp 169.
- (8) Elliott, D. C.; Baker, E. G.; Beckman, D.; Solantausta, Y.; Tulenheimo, V.; Östman, A.; Gevert, B.; Hörnell, C.; Kjellström, B. Technoeconomic Assessment of Direct Biomass Liquefaction to Transportation Fuels. In *Forestry, Forest Biomass, and Biomass Conversion: The IEA Bioenergy Agreement (1986–1989) Summary Reports*; Mitchell, C. P., Zsuffa, L., Andersson, S., Stevens, D. J., Eds.; Elsevier, London-New York, 1990; Vol. 22, Issue 1–4, pp 251–269.
- (9) Solantausta, Y.; Diebold, J. P.; Elliott, D. C.; Bridgwater, T.; Beckman, D. Assessment of liquefaction and pyrolysis systems. *VTT Research Notes*; VTT: Espoo, Finland, 1994; Vol. 1573, pp 123.
- (10) Diebold, J. P.; Bridgwater, A.; Beckman, D.; Elliott, D. C.; Solantausta, Y. IEA Technoeconomic Analysis of the Thermochemical Conversion of Biomass to Gasoline by the NREL Process. In *Advances in Thermochemical Biomass Conversion 2*; Bridgwater, A. V., Ed.; Blackie Academic & Professional: Glasgow, U.K., 1994; pp 1325–1342.
- (11) Scott, D. S.; Piskorz, J. The Flash Pyrolysis of Aspen-Poplar Wood. *Can. J. Chem. Eng.* **1982**, *60*, 666–674.
- (12) Arpiainen, V.; Lappi, M. Products from the flash pyrolysis of peat and pine bark. *J. Anal. Appl. Pyrolysis* **1989**, *16* (4), 355–376.
- (13) *Fast Pyrolysis of Biomass—A Handbook*; Bridgwater, A., Czernik, S., Diebold, J., Meier, D., Oasmaa, A., Peacocke, C., Piskorz, J., Radlein, D., Eds.; CPL Press: Newbury, U.K., 1999; ISBN 1-872691-07.
- (14) *Fast Pyrolysis of Biomass—A Handbook*; Bridgwater, A., Czernik, S., Diebold, J., Meier, D., Oasmaa, A., Peacocke, C., Piskorz, J., Radlein, D., Eds.; CPL Press: Newbury, U.K., 2002; Vol. 2, ISBN 9781872691473, pp 432.
- (15) *Fast Pyrolysis of Biomass—A Handbook*; Bridgwater, A., Czernik, S., Diebold, J., Meier, D., Oasmaa, A., Peacocke, C., Piskorz, J., Radlein, D., Eds.; CPL Press: Newbury, U.K., 2005; Vol. 3, ISBN 1872691927.
- (16) <https://task34.ieabioenergy.com/pyne-1996-2000/>; <https://task34.ieabioenergy.com/iea-publications/newsletters/pyne-1996-2005/>; <https://task34.ieabioenergy.com/pyne-2016-2019/>; <https://task34.ieabioenergy.com/books-and-proceedings/>.
- (17) Solantausta, Y.; Nylund, N.-O.; Westerholm, M.; Koljonen, T.; Oasmaa, A. Wood pyrolysis oil as fuel in a diesel power plant. *Bioresour. Technol.* **1993**, *46*, 177–188.
- (18) Jay, D. C.; Rantanen, O.; Sipilä, K.; Nylund, N.-O. Wood pyrolysis oil for diesel engines. *Proceedings of the 1995 Fall Technical Conference*; Milwaukee, WI, Sept 24–27, 1995.
- (19) Fagernäs, L. Chemical and physical characterisation of biomass-based pyrolysis oils: Literature Review. *VTT Research Notes*; VTT: Espoo, Finland, 1995; Vol. 1706, pp 113.
- (20) Oasmaa, A.; Leppämäki, E.; Koponen, P.; Levander, J.; Tapola, E. *Physical Characterisation of Biomass-Based Pyrolysis Liquids: Application of Standard Fuel Oil Analyses*; VTT: Espoo, Finland, 1997; Vol. 306, pp 46.
- (21) Oasmaa, A. Fuel oil quality properties of wood-based pyrolysis liquids. Academic Dissertation. University of Jyväskylä, Jyväskylä, Finland, 2003; pp 283.
- (22) Solantausta, Y. Cost and performance analysis of new wood-fuelled power plant concepts. Ph.D. Dissertation, Aston University, Birmingham, U.K., 2000.
- (23) Onarheim, K.; Solantausta, Y.; Lehto, J. Process simulation development of fast pyrolysis of wood using AspenPlus. *Energy Fuels* **2015**, *29* (1), 205–217.
- (24) Onarheim, K.; Lehto, J.; Solantausta, Y. Technoeconomic assessment of a fast pyrolysis bio-oil production process integrated to a fluidized bed boiler. *Energy Fuels* **2015**, *29* (9), 5885–5893.
- (25) Elliott, D. C. Catalytic hydroprocessing of bio-oils of different types. Ph.D. thesis. University of Groningen, The Netherlands 2019, <https://research.rug.nl/en/publications/catalytic-hydroprocessing-of-bio-oils-of-different-types>.
- (26) Lappas, A. A.; Kalogiannis, K. G.; Iliopoulou, E. F.; Triantafyllidis, K. S.; Stefanidis, S. D. Catalytic pyrolysis of biomass for transportation fuels. *WIREs Energy Environment* **2012**, *1*, 285–297.
- (27) Paasikallio, V.; Lindfors, C.; Kuoppala, E.; Solantausta, Y.; Oasmaa, A.; Lehto, J.; Lehtonen, J. Product quality and catalyst deactivation in a four day catalytic fast pyrolysis production run. *Green Chem.* **2014**, *16* (7), 3549–3559.
- (28) Wang, H.; Santosa, D. M.; Elliott, D. C.; Agblevor, F. A.; Lindfors, C. In Situ Catalytic Fast Pyrolysis and Hydrotreating to Convert Biomass. *Proceedings of the Spring 2018 255th ACS National Meeting*; New Orleans, LA, March 18–22, 2018.
- (29) Oasmaa, A.; Kuoppala, E.; Gust, S.; Solantausta, Y. Fast Pyrolysis of Forestry Residue. 1. Effect of Extractives on Phase Separation of Pyrolysis Liquids. *Energy Fuels* **2003**, *17*, 1–12.
- (30) Oasmaa, A.; Kuoppala, E.; Solantausta, Y. Fast Pyrolysis of Forestry Residue. 2. Physicochemical Properties of Pyrolysis Liquids. *Energy Fuels* **2003**, *17* (2), 433–443.
- (31) Oasmaa, A.; Kuoppala, E. Fast pyrolysis of forestry residue. 2003. Storage stability of liquid fuel. *Energy Fuels* **2003**, *17* (4), 1075–1084.
- (32) Oasmaa, A.; Kuoppala, E.; Selin, J.-F.; Gust, S.; Solantausta, Y. Fast Pyrolysis of Forestry Residue and Pine. 4. Improvement of the Product Quality by Solvent Addition. *Energy Fuels* **2004**, *18*, 1578–1583.
- (33) Pienhäkkinen, E.; Lindfors, C.; Ohra-Aho, T.; Granström, T.; Oasmaa, A.; Lehtonen, J.; Yamamoto, M. Fast pyrolysis of hydrolysis lignin in fluidized bed. *PyNe Newsl.* **2020**, 46.
- (34) Fonts, I.; Kuoppala, E.; Oasmaa, A. Physicochemical properties of product liquid from pyrolysis of sewage sludge. *Energy Fuels* **2009**, *23* (8), 4121–4128.
- (35) Elliott, D.; Baker, E.; Piskorz, J.; Scott, D.; Solantausta, Y. Production of liquid hydrocarbon fuels from peat. *Energy Fuels* **1988**, *2*, 234–235.

- (36) Oasmaa, A.; Boocock, D. G. B. The catalytic hydrotreatment of peat pyrolysate oils. *Can. J. Chem. Eng.* **1992**, *70* (2), 294–300.
- (37) Qureshi, M. S.; Oasmaa, A.; Pihkola, H.; Deviatkin, I.; Tenhunen, A.; Mannila, J.; Minkinen, H.; Pohjakallio, M.; Laine-Ylijoki, J. Pyrolysis of plastic waste: Opportunities and challenges. *J. Anal. Appl. Pyrolysis* **2020**, *152*, 104804.
- (38) Bridgwater, A. V. Fast pyrolysis of biomass. In *Thermal Biomass Conversion*; Bridgwater, A. V., Hofbauer, H., van Loo, S., Eds.; CPL Press: Newbury, U.K., 2009.
- (39) Rossi, C. The Bastardo pyrolysis plant for bio-oil production from biomass. *PyNe Newsl.* **1996**, *2*, 6–7. <https://task34.ieabioenergy.com/wp-content/uploads/sites/3/2016/10/PyNe-Issue-2.pdf>
- (40) Cuevas, A. The Production and Handling of WFPP Bio-oil and Its Implications for Combustion (Union Fenosa). *Proceedings of the Biomass Pyrolysis Oil Properties and Combustion Meeting*; Estes Park, CO, Sept 26–28, 1994; pp 151–156, NREL-CP-430-7215, [https://digital.library.unt.edu/ark:/67531/metadc871878/m2/1/high\\_res\\_d/1114056.pdf](https://digital.library.unt.edu/ark:/67531/metadc871878/m2/1/high_res_d/1114056.pdf).
- (41) Nieminen, J.-P.; Gust, S.; Nyrönen, T. Forestera liquefied wood fuel pilot plant. *PyNe Newsl.* **2003**, *16*, 2–4. <https://task34.ieabioenergy.com/wp-content/uploads/sites/3/2016/10/PyNews-16.pdf>
- (42) Solantausta, Y.; Oasmaa, A.; Sipilä, K.; Lindfors, C.; Lehto, J.; Autio, J.; Jokela, P.; Alin, J.; Heiskanen, J. Bio-oil production from biomass: Steps toward demonstration. *Energy Fuels* **2012**, *26* (1), 233–240.
- (43) btgbioliquids. <https://www.btg-btl.com/en>.
- (44) Ensyn. <http://www.ensyn.com/>.
- (45) Ratinen, S.; Lehto, J.; Anttila, M.; Hilli, T.; Onarheim, K.; Hirvonen, I.; Solantausta, Y.; Raiko, M. Method and apparatus for producing a pyrolysis product. U.S. Patent 8,668,811 B2, March 11, 2014.
- (46) Sipilä, K.; Solantausta, Y.; Jokela, P.; Raiko, M. Apparatus for producing a pyrolysis liquid. WO Patent 2009047392 A1, April 16, 2009.
- (47) Sipilä, K.; Solantausta, Y.; Jokela, P.; Raiko, M. Method for carrying out pyrolysis. WO Patent 2009047387 A1, April 16, 2009.
- (48) Lehto, J.; Jokela, P.; Oasmaa, A.; Solantausta, Y. Integrated heat, electricity and bio-oil production. *Biofuels Innovator* **2010**, 20–22.
- (49) Lehto, J.; Jokela, P.; Alin, J.; Solantausta, Y.; Oasmaa, A. Bio-oil Production Integrated with a Fluidized Bed Boiler—Experiences from a Pilot Project. *Best Papers Awards 2010: PEI Power Engineering* **2010**, 182–187.
- (50) Sipilä, E.; Vasara, P.; Sipilä, K.; Solantausta, Y. Feasibility and market potential of pyrolysis oils in European pulp and paper industry. *Proceedings of the 15th European Biomass Conference and Exhibition*; Berlin, Germany, May 7–11, 2007; ETA-WIP.
- (51) Fortum. *Fortum Biomass Plant Turned on in Finland 2013*; Fortum: Joensuu, Finland, Dec 2, 2013; <https://www.power-grid.com/der-grid-edge/fortum-biomass-plant-turned-on-in-finland/#gref>.
- (52) Valmet Oyj. *Valmet and Fortum Take Development of Bio-oil into Transportation Fuels to New Level in Collaboration with Preem*; Valmet Oyj: Espoo, Finland, April 10, 2018; <https://www.valmet.com/media/news/press-releases/2018/valmet-and-fortum-take-development-of-bio-oil-into-transportation-fuels-to-new-level-in-collaboration-with-preem/>.
- (53) Oasmaa, A.; Kuoppala, E. Solvent fractionation method with Brix for rapid characterization of wood fast pyrolysis liquids. *Energy Fuels* **2008**, *22* (6), 4245–4248.
- (54) Oasmaa, A.; Sundqvist, T.; Kuoppala, E.; Garcia-Perez, M.; Solantausta, Y.; Lindfors, C.; Paasikallio, V. Controlling Phase Stability of Biomass Fast Pyrolysis Bio-oils. *Energy Fuels* **2015**, *29*, 4373–4381.
- (55) Oasmaa, A.; Fonts, I.; Pelaez-Samaniego, M. R.; Garcia-Perez, M. E.; Garcia-Perez, M. Pyrolysis oil multiphase behavior and phase stability: A review. *Energy Fuels* **2016**, *30* (8), 6179–6200.
- (56) Oasmaa, A.; Solantausta, Y.; Arpiainen, V.; Kuoppala, E.; Sipilä, K. Fast Pyrolysis Bio-Oils from Wood and Agricultural Residues. *Energy Fuels* **2010**, *24* (2), 1380–1388.
- (57) Carpenter, D.; Westover, T. L.; Czernik, S.; Jablonski, W. Biomass feedstocks for renewable fuel production: A review of the impacts of feedstock and pretreatment on the yield and product distribution of fast pyrolysis bio-oils and vapors. *Green Chem.* **2014**, *16*, 384–406.
- (58) Evans, R. J.; Milne, T. A. Mass Spectroscopic Studies of the Relationship of Pyrolysis Oil Composition to Formation Mechanisms and Feedstock Composition. In *Research in Thermochemical Biomass Conversion*; Bridgwater, A. V., Kuester, J. L., Eds.; Elsevier Applied Science: Essex, U.K., 1988; pp 264–279.
- (59) Diebold, J. P.; Scahill, J. W.; Czernik, S.; Phillips, D.; Feik, C. J. *Progress in the Production of Hot-Gas Filtered Biocrude Oil at NREL*; National Renewable Energy Laboratory (NREL): Golden, CO, 1995; Technical Report NREL/TP-431-7971.
- (60) Ringer, M.; Putsche, V.; Scahill, J. *Large-Scale Pyrolysis Oil Production: A Technology Assessment and Economic Analysis*; National Renewable Energy Laboratory (NREL): Golden, CO, 2006; Technical Report NREL/TP-510-37779.
- (61) Wang, H.; Elliott, D. C.; French, R. J.; Deutch, S.; Iisa, K. Biomass Conversion to Produce Hydrocarbon Liquid Fuel Via Hot-Vapor Filtered Fast Pyrolysis and Catalytic Hydrotreating. *J. Vis. Exp.* **2016**, *118*, No. 54088.
- (62) Oh, S.; Choi, I.-G.; Choi, J. W. Pretreatment of bio-oil with ion exchange resin to improve fuel quality and reduce char during hydrodeoxygenation upgrading with Pt/C. *Environ. Technol.* **2021**, *42* (7), 1132–1144.
- (63) Zhou, G.; Roby, S. Study on the Removal of Metals from Pyrolysis Oil with Ion-Exchange Resins at Ambient Conditions. *Energy Fuels* **2016**, *30* (2), 1002–1005.
- (64) Ratinen, S.; Solantausta, Y.; Nieminen, M.; Lindfors, C.; Källi, A. Apparatus and method for cleaning a stream. U.S. Patent 20200061513 A1, 2019.
- (65) Diebold, J. P. A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-oils. In *Fast Pyrolysis of Biomass: A Handbook*; Bridgwater, A. V., Ed.; CPL Press: Newbury, U.K., 2002; pp 243–292.
- (66) Czernik, S.; Johnson, D. K.; Black, S. Stability of Wood Fast Pyrolysis Oil. *Biomass Bioenergy* **1994**, *7* (1–6), 187–192.
- (67) Oasmaa, A. *Bio-oil Stabilization, Fast Pyrolysis of Biomass: Advances in Science and Technology*; Royal Society of Chemistry (RSC): London, U.K., 2017; pp 138–159, DOI: 10.1039/9781788010245-00138.
- (68) Fratini, E.; Bonini, M.; Oasmaa, A.; Solantausta, Y.; Teixeira, J.; Baglioni, P. SANS Analysis of the Microstructural Evolution during the Aging of Pyrolysis Oils from Biomass. *Langmuir* **2006**, *22* (1), 306–312.
- (69) Li, M.; Yu, Y.; Wu, H. Effect of Single/Mixed Model Solvents on the Ternary Phase Diagrams of Pyrolytic Lignin, Model Solvent, and Water. *Energy Fuels* **2020**, *34* (12), 15355–15369.
- (70) Sundqvist, T.; Solantausta, Y.; Oasmaa, A.; Kokko, L.; Paasikallio, V. Heat generation during the aging of wood-derived fast-pyrolysis bio-oils. *Energy Fuels* **2016**, *30* (1), 465–472.
- (71) Chiaramonti, D.; Oasmaa, A.; Solantausta, Y.; Peacocke, C. The use of biomass derived fast pyrolysis liquids in power generation: Engines and turbines. *Power Engineer* **2007**, *11* (5), 3–25.
- (72) Chiaramonti, D.; Oasmaa, A.; Solantausta, Y. Power generation using fast pyrolysis liquids from biomass. *Renewable Sustainable Energy Rev.* **2007**, *11*, 1056–1086.
- (73) Solantausta, Y.; Mäkinen, T.; McKeough, P.; Kurkela, E. Performance of Cogeneration Gasification Combined-Cycle Power Plants Employing Biomass as Fuel. *Adv. Thermochem. Biomass Convers.* **1993**, 476–494.
- (74) Lehto, J.; Oasmaa, A.; Solantausta, Y.; Kytö, M.; Chiaramonti, D. Fuel oil quality and combustion of fast pyrolysis bio-oils. *VTT Technol.* **2013**; Vol. 87, pp 79, <http://www.vtt.fi/inf/pdf/technology/2013/T87.pdf>.
- (75) Lehto, J.; Oasmaa, A.; Solantausta, Y.; Kytö, M.; Chiaramonti, D. Review of fuel oil quality and combustion of fast pyrolysis bio-oils from lignocellulosic biomass. *Appl. Energy* **2014**, *116*, 178–190.

- (76) Lindfors, C.; Oasmaa, A.; Välimäki, A.; Ohra-Aho, T.; Punkkinen, H.; Bajamundi, C.; Onarheim, K. Standard liquid fuel for industrial boilers from used wood. *Biomass Bioenergy* **2019**, *127*, 105265.
- (77) Koivusalo, V. "Otso" Bio-oil; Fortum: Joensuu, Finland, 2016; <https://wiki.uefi.fi/pages/viewpage.action?pageId=41911703>.
- (78) Zacher, A. H.; Elliott, D. C.; Olarte, M. V.; Wang, H.; Jones, S. B.; Meyer, P. A. Technology advancements in hydroprocessing of bio-oils. *Biomass Bioenergy* **2019**, *125*, 151–168.
- (79) Si, Z.; Zhang, X.; Wang, C.; Ma, L.; Dong, R. An Overview on Catalytic Hydrodeoxygenation of Pyrolysis Oil and Its Model Compounds. *Catalysts* **2017**, *7*, 169.
- (80) Stankovikj, F.; Tran, C. C.; Kaliaguine, S.; Olarte, M. V.; Garcia-Perez, M. Evolution of functional groups during pyrolysis oil upgrading. *Energy Fuels* **2017**, *31* (8), 8300–8316.
- (81) Oasmaa, A.; Sipilä, K.; Solantausta, Y.; Kuoppala, E. Quality improvement of pyrolysis liquid: Effect of light volatiles on the stability of pyrolysis liquids. *Energy Fuels* **2005**, *19* (6), 2556–2561.
- (82) Oasmaa, A.; Elliott, D. C.; Korhonen, J. Acidity of biomass fast pyrolysis bio-oils. *Energy Fuels* **2010**, *24* (12), 6548–6554.
- (83) Lindfors, C.; Kuoppala, E.; Oasmaa, A.; Solantausta, Y.; Arpiainen, V. Fractionation of bio-oil. *Energy Fuels* **2014**, *28* (9), 5785–5791.
- (84) Sundqvist, T.; Oasmaa, A.; Koskinen, A. Upgrading fast pyrolysis bio-oil quality by esterification and azeotrop water removal. *Energy Fuels* **2015**, *29* (4), 2527–2534.
- (85) Paasikallio, V.; Lindfors, C.; Lehto, J.; Oasmaa, A.; Reinikainen, M. Short vapour residence time catalytic pyrolysis of spruce sawdust in a bubbling fluidized-bed reactor with HZSM-5 catalysts. *Top. Catal.* **2013**, *56* (9–10), 800–812.
- (86) Paasikallio, V.; Lindfors, C.; Kuoppala, E.; Solantausta, Y.; Oasmaa, A.; Lehto, J.; Lehtonen, J. Product quality and catalyst deactivation in a four day catalytic fast pyrolysis production run. *Green Chem.* **2014**, *16* (7), 3549–3559.
- (87) Paasikallio, V.; Agblevor, F.; Oasmaa, A.; Lehto, J.; Lehtonen, J. Catalytic pyrolysis of forest thinnings with ZSM-5 catalysts: Effect of reaction temperature on bio-oil physical properties and chemical composition. *Energy Fuels* **2013**, *27* (12), 7587–7601.
- (88) Lindfors, C.; Paasikallio, V.; Kuoppala, E.; Reinikainen, M.; Oasmaa, A.; Solantausta, Y. Co-processing of dry bio-oil, catalytic pyrolysis oil, and hydrotreated bio-oil in a micro activity test unit. *Energy Fuels* **2015**, *29* (6), 3707–3714.
- (89) Ratinen, S.; Solantausta, Y.; Nieminen, M.; Lindfors, C.; Källi, A. Apparatus and method for cleaning a stream with a moving bed. WO Patent 2018206851 A1, 2018.
- (90) Solantausta, Y. Biofuel oil—Upgrading by hot filtration and novel physical methods. *Pyrolysis Network (PyNe)* **2000**, *9*, 8–9.
- (91) Elliott, D. C. Historical developments in hydroprocessing bio-oils. *Energy Fuels* **2007**, *21*, 1792–1815.
- (92) Oasmaa, A.; Kuoppala, E.; Ardiyanti, A.; Venderbosch, R. H.; Heeres, H. J. Characterization of hydrotreated fast pyrolysis liquids. *Energy Fuels* **2010**, *24* (9), 5264–5272.
- (93) Oasmaa, A.; Källi, A.; Lindfors, C.; Elliott, D. C.; Springer, D.; Peacocke, C.; Chiaramonti, D. Guidelines for transportation, handling, and use of fast pyrolysis bio-oil. 1. Flammability and toxicity. *Energy Fuels* **2012**, *26*, 3864–3873.
- (94) Sipilä, K.; Kuoppala, E.; Fagernäs, L.; Oasmaa, A. Characterization of Biomass-Based Flash Pyrolysis Oils. *Biomass Bioenergy* **1998**, *14*, 103–113.
- (95) Oasmaa, A.; Korhonen, J.; Kuoppala, E. An approach for stability measurement of wood-based fast pyrolysis bio-oils. *Energy Fuels* **2011**, *25*, 3307–3313.
- (96) Oasmaa, A.; Kuoppala, E.; Elliott, D. C. Development of the basis for an analytical protocol for feeds and products of bio-oil hydrotreatment. *Energy Fuels* **2012**, *26* (4), 2454–2460.
- (97) Oasmaa, A.; Peacocke, C. *A Guide to Physical Property Characterisation of Biomass-Derived Fast Pyrolysis Liquids*; VTT: Espoo, Finland, 2001; Vol. 450, pp 65, <http://www.vtt.fi/inf/pdf/publications/2001/P450.pdf>.
- (98) Oasmaa, A.; Meier, D. Norms and standards for fast pyrolysis liquids 1. Round robin test. *J. Anal. Appl. Pyrolysis* **2005**, *73* (2), 323–334.
- (99) Elliott, D. C.; Oasmaa, A.; Preto, F.; Meier, D.; Bridgwater, A. V. Results of the IEA round robin on viscosity and stability of fast pyrolysis bio-oils. *Energy Fuels* **2012**, *26*, 3769–3776.
- (100) Elliott, D. C.; Oasmaa, A.; Meier, D.; Preto, F.; Bridgwater, A. V. Results of the IEA round robin on viscosity and aging of fast pyrolysis bio-oils: Long-Term tests and repeatability. *Energy Fuels* **2012**, *26* (12), 7362–7366.
- (101) Elliott, D. C.; Meier, D.; Oasmaa, A.; van de Beld, B.; Bridgwater, A.; Marklund, M. Results of the International Energy Agency round robin on fast pyrolysis bio-oil production. *Energy Fuels* **2017**, *31* (5), 5111–5119.
- (102) Bulsink, P.; de Miguel Mercader, F.; Sandström, L.; van de Beld, B.; Preto, F.; Zacher, A.; Oasmaa, A.; Dahmen, N.; Funke, A.; Bronson, B. Results of the International Energy Agency Bioenergy Round Robin on the Analysis of Heteroatoms in Biomass Liquefaction Oils. *Energy Fuels* **2020**, *34*, 11123–11133.
- (103) Oasmaa, A.; Czernik, S. Fuel oil quality of biomass pyrolysis oils. State of the art for the end users. *Energy Fuels* **1999**, *13* (4), 914–921.
- (104) Gust, S.; McLellan, R. J.; Oasmaa, A.; Ormrod, D.; Peacocke, G. V. C. Determination of norms and standards for bio-oil as an alternative renewable fuel for electricity and heat production. In *Fast Pyrolysis of Biomass: A Handbook*; Bridgwater, A. V., Ed.; Bio-Energy Research Group, Aston University: Birmingham, U.K., 2005, Vol. 3, pp 9–18.
- (105) Oasmaa, A.; Peacocke, C.; Gust, S.; Meier, D.; McLellan, R. Norms and Standards for Pyrolysis Liquids. End-User Requirements and Specifications. *Energy Fuels* **2005**, *19* (5), 2155–2163.
- (106) Oasmaa, A.; Elliott, D. C.; Müller, S. Quality Control in Fast Pyrolysis Bio-Oil Production and Use. *Environ. Prog. Sustainable Energy* **2009**, *28* (3), 404–409.
- (107) Oasmaa, A.; Van De Beld, B.; Saari, P.; Elliott, D. C.; Solantausta, Y. Norms, standards, and legislation for fast pyrolysis bio-oils from lignocellulosic biomass. *Energy Fuels* **2015**, *29* (4), 2471–2484.
- (108) Oasmaa, A.; Venderbosch, R.; Ohra-Aho, T. Bio-liquids for Co-refining—Determination of Quality. *Proceedings of the ACS Fall 2020 Virtual Meeting & Expo*; Aug 17–20, 2020.
- (109) Mellow, E.; Chapel, S.; Worthing, C. *A Review of Cost Estimation in New Technologies: Implications for Energy Process Plants*; RAND Corporation: Santa Monica, CA, 1979; RAND-R-2481-DOE.
- (110) Mellow, E.; Phillips, K.; Myers, C. *Understanding Cost Growth and Performance Shortfalls in Pioneer Process Plants*; RAND Corporation: Santa Monica, CA, 1981; R-2569-DOE.
- (111) Sorsa, R. Hakkuutähteestä valmistetun pyrolyysiöljyn elinkaaren kasviuonekaasupäästöt (The Life Cycle Assessment of Pyrolysis Oil Derived from Logging Residues). Master's Thesis, Energy Technology, Faculty of Technology, Lappeenranta University of Technology, Lappeenranta, Finland, 2011.
- (112) Ranzi, E.; Cuoci, A.; Faravelli, T.; Frassoldati, A.; Migliavacca, G.; Pierucci, S.; Sommariva, S. Chemical kinetics of biomass pyrolysis. *Energy Fuels* **2008**, *22* (6), 4292–4300.
- (113) Kostetskyy, P.; Broadbelt, L. J. Progress in Modeling of Biomass Fast Pyrolysis: A Review. *Energy Fuels* **2020**, *34*, 15195–15216.
- (114) Ding, J.; Gidaspow, D. A bubbling fluidization model using kinetic theory of granular flow. *AIChE J.* **1990**, *36*, 523–538.
- (115) Taivassalo, V.; Kallio, S.; Peltola, J. On time-averaged CFD modeling of circulating fluidized beds. *Int. J. Nonlinear Sci. Numer. Simul.* **2012**, *13*, 363–373.
- (116) Wang, G.; Dai, Y.; Yang, H.; Xiong, Q.; Wang, K.; Zhou, J.; Li, Y.; Wang, S. A Review of Recent Advances in Biomass Pyrolysis. *Energy Fuels* **2020**, *34*, 15557–15578.
- (117) Oasmaa, A.; Minkinen, H.; Lindfors, C.; Lehto, J.; Mannila, J. Method of carrying out thermolysis and thermolysis apparatus. US2020/0398475A1, December 24, 2020.