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Fast Pyrolysis Bio-Oils from Wood and Agricultural Residues

Anja Oasmaa,* Yrjö Solantausta, Vesa Arpiainen, Eeva Kuoppala, and Kai Sipilä

VTT, P.O. Box 1000, 02044 VTT, Finland

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Fast pyrolysis bio-oil (pyrolysis liquid) from plant residues is one alternative to replace fossil fuels and feedstocks. Fast pyrolysis liquid is a potential source of revenues for companies who have biomass residues at their disposal. Once produced, bio-oils may be shipped, stored, and utilized much like conventional liquid fuels once their specific fuel properties are taken into account. First encouraging large scale bio-oil utilization tests with published results were carried out in Stockholm in the 1990s in a heating boiler designed for heavy fuel oil. Industrial ovens are also potential users of bio-oil. Bio-oil would also be an interesting fuel for small scale distributed heat or power production. However, introducing a new fuel into the markets is not going to happen easily. Bio-oil is quite different from conventional liquid fuels, and many challenges remains to be overcome. A stepwise market introduction is proposed: bio-oil would first replace fuel oil in boilers, where its properties would not be prohibitive. Once the overall utilization chain has been proven, more demanding uses may be introduced. VTT has been developing an integrated concept, in which fast pyrolysis is integrated to a fluidized-bed boiler. The experimental work on fast pyrolysis has been focused in supporting this concept. In Scandinavia, forest residues are the most feasible feedstocks for pyrolysis. These residues contain extractive matter that yield a second liquid phase. This is both an opportunity (for recovering byproduct) and a challenge (for using both phases as fuel). Agro-biomasses are more challenging feedstocks for energy use due to the high amount of alkali metals and nitrogen in the oil. In addition, they produce more water during pyrolysis, causing phase instability. In this paper, fast pyrolysis is discussed including experimental results from pyrolysis of wood and agricultural residues as well as results from a techno-economic evaluation.

Introduction

The focus of this paper is to provide information concerning one strategic approach to commercialize bio-oil production with fast pyrolysis. The paper contains results of the work carried out at VTT during development of this biofuel utilization chain.

Potential Uses for Bio-Oil. Bio-oils from plant residues is one alternative to replace fossil fuels and feedstocks. Use of bio-oil in industrial kilns, boilers, diesel engines, and gas turbines has been tested. Further uses in production of chemicals and feedstock for synthesis gas production (and further production of transportation fuels and C1-chemicals) are also developed. Bio-oil has also been upgraded in small scale to transportation fuel fractions. However, currently the only commercial use of bio-oil is in food flavouring industry.¹

Bio-oil, which is frequently also referred to as bio crude, fast pyrolysis oil, flash pyrolysis oil, or pyrolysis liquid, is a potential source of revenues for companies who have biomass residues at their disposal. Such biomasses are, for example, forest residues, forest industry residues, and some agricultural residues such as straw. It has been estimated that especially agricultural residues are a considerable potential source, although it is typically hard to accumulate them with a competitive cost in large quantities at one location.

Once produced, bio-oils may be shipped, stored, and utilized much like conventional liquid fuels once their specific fuel properties are taken into account. Current bio-oil qualities experienced in test use over the years have been considerably

variable. However, once more large scale experiences are available, specific properties of bio-oils will be better understood, and proper utilization procedures will be developed.

First encouraging large scale bio-oil utilization tests with published results² were carried out in Stockholm in the 1990s in a heating boiler designed for heavy fuel oil. Several different well-defined bio-oils were subsequently tested with good results in an industrial scale boiler.³ Laboratory combustion tests had already been carried out earlier with bio-oils, but often oils used could not be considered industrially relevant due to the small scale of production facilities at the time. Since then, much progress has been achieved in using bio-oil, for example, in small scale (300–1000 kW) heat boilers designed for light fuel oil,⁴ in which bio-oil was used in automatic operation for one heating season. Bio-oil has also been cofired in a large natural gas boiler,⁵ an application technically less demanding than a small boiler.

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(3) Oasmaa, A.; Kytö, M.; Sipilä, K. Pyrolysis Oil Combustion Tests in an Industrial Boiler. In *Progress in Thermochemical Biomass Conversion*; Bridgwater, A. V. Ed.; Blackwell Science: Oxford, 2001; Vol. 2, pp 1468–1481.

(4) Kytö, M.; Martin, P.; Gust, S. Development of combustors for pyrolysis liquids. In: *Pyrolysis and Gasification of Biomass and Waste*, Strasbourg, France, Sept. 30 to Oct. 1, 2002; Bridgwater, A. V. Ed.; CPL Press: Newbury, UK, 2003; pp 187–190.

(5) Wagenaar, B. M.; Gansekoele, E.; Florijn, J.; Venderbosch, R. H.; Penninks, F. W. M.; Stellingwerf, A. Bio-oil as natural gas substitute in a 350 MWe power station. In *2nd World Conference on Biomass for Energy, Industry and Climate Protection*, May 10–14, 2004, Rome, Italy, 2004.

*Corresponding author: Anja.Oasmaa@vtt.fi.

(1) Underwood, G.; Graham, R. G. *Method of using fast pyrolysis liquids as liquid smoke*. US Patent No. 4,876,108; October 24, 1989.

Industrial ovens are also potential users of bio-oil. At least short duration lime kiln tests have been carried out, however, not much results have been made available.

Bio-oil would also be an interesting fuel for small scale distributed power production.⁶ Currently, biogas or bio-oils are only feasible bio fuels available in small scale for internal combustion engines or microturbines, but they suffer from high costs. In addition, digested biogas and thermally produced biogas typically has to be used close to gas production. Ethanol, the most commonly available liquid biofuel, is considered too expensive for power production. Solid biomasses are competitive without some financial support only in large scale power production (steam-cycle Rankine power plants typically above 30–50 MW electrical), if low cost biomass is available. In combined-heat-and-power (CHP) production even smaller scale plants may be viable, but seldom below 5 MW electrical. Diesel engine tests with bio-oils have been carried out from the early 1990s.^{7,8} However, so far no breakthrough has been reporting in overcoming some of the more challenging aspects of utilization, including wear of injection equipment.

Use of bio-oil in a gas turbine has been developed especially by Orenda⁹ since the mid-90s. They have converted an existing engine to be used for bio-oil, and one unit has been installed at a bio-oil production facility in Canada.¹⁰ However, little information is available on the continuous use of the engine.

A liquid bio fuel concept, where widely distributed biomass (straw) is employed, is under development in Germany.¹¹ In the concept, bio-oil/char slurries are produced in 40 distributed pyrolysis plants, and the bio-oil slurry is transported to a large centralized gasification Fischer–Tropsch facility producing 1 Mt/a of hydrocarbon biofuel (Biomass to Liquid, BtL). Bio-oil could also be a complementary fuel to a large central facility. It is well-known that if liquid biofuels will be produced in large amounts, the competition on biomass feedstocks will intensify. In this case a feasible scenario is to transport many different (bio)fuels to a single gasification plant. Feasibility of transporting different biomass fuels has been analyzed among others by the ECN.¹²

A process concept originally proposed at PNNL in the 1980s is aimed at upgrading bio-oil to transportation fuels.¹³ Isolated batch laboratory work in universities has been carried out since then. However, the same challenge as in bio-oil combustion research hampered the work: oils used could not be considered industrially relevant due to the small

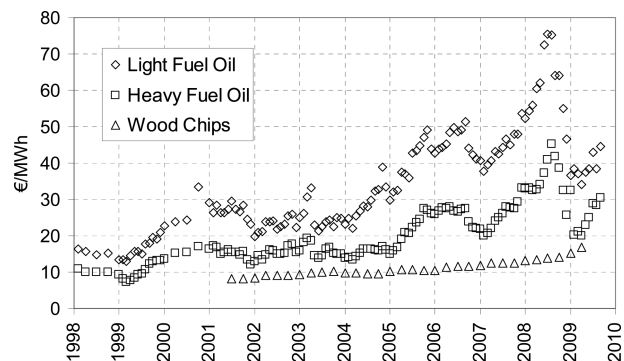


Figure 1. Non-taxed fuel oil and wood chip prices in Finland.

scale of bio-oil production facilities, or because their history was not really known due to chemical changes in storage, or uncertainty concerning their representativeness. However, at least part of early bench scale continuous tests carried out by Veba Oel were carried out with a bio-oil of known history during the 1990s.¹⁴ Veba Oel was trying to upgrade bio-oil so that it could be fed to a conventional refinery. PNNL has published a series of results on hydrodeoxygenation (HDO) of bio-oils with promising results. A comprehensive review has since been published,¹⁵ which includes all the important work in the area. Lately, bio-oil upgrading has again received more attention. Among others, a European project has been established with basically the same aim, which Veba Oel was working on in the 90s.¹⁶

Over the years, attention has also been paid on the possibility to produce various chemicals from bio-oils. A review on this area has been published.¹⁷ There has been an increased interest recently on the possibility to produce chemicals from bio-oil.

Biomass Cost, Availability, and Fuel Oil Price. Introducing a new fuel, for example bio-oil, into the markets is not going to happen easily. Bio-oil is quite different from conventional liquid fuels, and many challenges remain to be overcome. A stepwise market introduction is proposed: bio-oil would first replace fuel oil in boilers, where its properties would not be prohibitive. An example of such a chain has been presented earlier.¹⁸ Once the whole chain from biomass to fast pyrolysis plant to heat utilization has been proven, other uses may be demonstrated. To illustrate the initial markets, fuel oil and wood chip prices in Finland are shown in Figure 1 below. Oil prices are representative for Europe. Wood chips prices are less so, because in only a few countries outside Scandinavia are established market prices for fuel biomass available. The Finnish wood prices may be considered real market prices, as there is a large established consumption for boilers.

It may be seen that especially since around 2005 the difference between fuel oil and wood prices has increased.

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(11) Henrich, E.; Dahmen, N.; Dinjus, E. *Biofuels, Bioprod. Bioref.* **2009**, *3*, 28–41.

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(16) Solantausta, Y. Co-processing of Upgraded Bio-Liquids in Standard Refinery Units - BIOCOUP. In *European Conference on Biorefinery Research*, Helsinki, Oct. 19–20, 2006.

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This widening difference provides, in principle, an incentive to produce bio-oil from wood.

It is well-known that there is currently competition of good quality biomasses for fuel use. Biomass is especially popular in power production, where market incentives are in place in many EU countries to produce green electricity. Power plants will remain large users of wood fuels, as for example modern fluidized-bed boilers may use several types of biomasses. To be able to compete on the markets, bio-oil production must be able to provide a higher payoff for the investor than current alternatives.

Bio-oil production potential in the European pulp and paper (PP) industry has been analyzed by Sipilä et al.¹⁹ The European PP industry has a potential to build up to 50 pyrolyzers integrated to fluidized-bed boilers. In the short term, the pyrolysis oil market is in fuel oil and natural gas replacement in lime kilns and boilers. The challenge is to develop and demonstrate a technical and economic concept for these applications.

Bio-oil Production Technologies. A review article is available for alternatives being developed for bio-oil production,²⁰ and only a brief summary is given below with an emphasis on the potential of reducing production costs.

Developments in fast pyrolysis may be traced back to a development program by Occidental Petroleum, which took place in the US during late 1960s and early 70s. However, most important development work on this field is in debt to the development in University of Waterloo, Canada, by Professor Scott and his co-workers. The modern understanding of fast pyrolysis is based largely on their pioneering work (e.g., ref 21 and several subsequent publications). Another important development was started at the University of Western Ontario, which eventually led to the establishing of Ensyn Technologies.²² Considerable early fundamental work was also carried out at NREL in the U.S. (e.g., ref 23). In Europe, development work initiated at the University of Twente, The Netherlands, has led to a process development at BTG.

Some major development paths since 1990 of bio-oil production are illustrated in Figure 2. Developments to produce food flavourings are outside the scope of this survey. Before about 1990, work was carried out only in bench scale. Currently a few companies are pushing to commercialize bio-oil for energy applications: Ensyn Technologies, Dynamotive, Forschungszentrum Karlsruhe (FZK), and BTG have probably most advanced initiatives to pursue larger scale operations.

VTT in Finland has been developing an integrated concept, in which fast pyrolysis is integrated to a fluidized-bed boiler (Figure 3). Extra biofuels (compared to existing heat loads) are often available at sites, where combined-heat-and-power (CHP) is produced (district heating plants, forest industry sites). The alternative for using the extra bio fuel

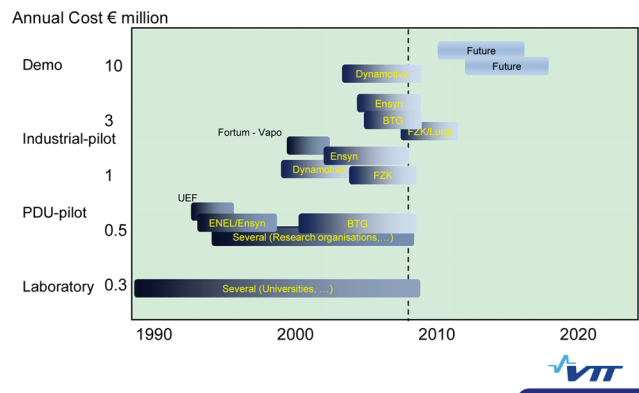


Figure 2. Development paths of fast pyrolysis for energy applications. Costs adjusted to 2008 level.

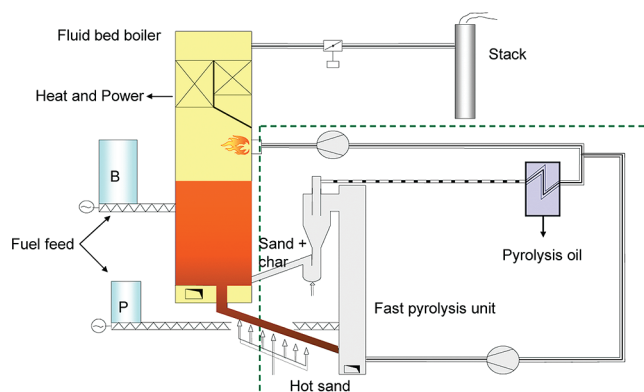


Figure 3. Integrated pyrolysis.

for the CHP plant is to generate more power with a partly condensing turbine. However, condensing head of a steam turbine has only a total efficiency of about 25–30%, whereas bio-oil may be exported from the site to high value users.

The integration is considered to bring in technical and economic advantages: (1) a high overall efficiency compared to stand-alone pyrolysis concepts; (2) lower investment costs due to no need for a specific char combustor (effects to the cost of the main boiler are considered marginal); (3) lower operating costs than stand-alone pyrolysis due to reduced man-power; (4) operating flexibility due to full exploitation of byproduct in the main boiler; and (5) operation is easier, because there is no need to combust byproduct char in a small suboptimal boiler, which often would be needed to generate plant energy requirements.

Metso has built the world's first integrated pyrolysis pilot plant (300 kg/h) in Finland, in co-operation with UPM and VTT.²⁴ A fast pyrolysis unit is integrated with a fluidized bed boiler as described above. As part of the project, a novel wood-based bio-oil concept will be developed. The related concept covers the entire business chain, from feedstock purchase and pretreatment to bio-oil production, transportation, storage, and end use.

Experimental Section

Feedstocks. Wood feedstocks used were pine saw dust (*Pinus sylvestris*), various forest fuels (fresh and stored forest residue

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Table 1. Biomass Feedstock Properties

	method	unit	pine	forest residue (FR)						RCG
				brown/stored	green/fresh	euca	barley straw	rapeseed straw	timothy hay	
moisture as received	DIN 51718	wt %	9.5	4.9	8.1	7.6	8.8	10.0	3.9	10.9
ash, dm	DIN 51719	wt %	0.1	3.8	2.1	0.4	5.8	6.1	3.2	1.1
volatiles, dm	DIN 51720	wt %	84	73.2	76.7	82.7	73.9	77.5	76.7	81.3
carbon, dm	ASTM D 5373	wt %	50.5	51.1	51.4	50.1	48.8	46.4	47.6	45.7
hydrogen, dm	ASTM D 5373	wt %	6.4	5.9	6	6	5.9	5.9	6.1	5.6
nitrogen, dm	ASTM D 5373	wt %	<0.1	0.5	0.5	0.1	0.8	0.5	0.7	0.9
oxygen, dm	as difference	wt %	43	43	42	44	45	47	46	48
O/C		mol/mol	0.85	0.83	0.82	0.87	0.91	1.02	0.96	1.05
H/C		mol/mol	0.13	0.12	0.12	0.12	0.12	0.13	0.13	0.12
HHV, dm	DIN 51900	MJ/kg	20.4	20.5	20.8	19.9	18.5	18.5	19.1	19.7
LHV, dm	DIN 51901	MJ/kg	17.0	19.3	19.5	18.6	17.2	17.2	17.8	18.5
pyrolysis scale		kg/h	20	20	20	20	1	1	1/20	1
20 kg/h/1 kg/h										
> 5/> 6	sieves	mm	1/0	0.2	0.6	0.1	0	0	8/0	0
3–5/4–6		mm	5/0	2	16	2.2	0	0	16.5/0	0
2–3/2–4		mm	14/0	33	54	42	0.4	0.3	20/1	0.3
1–2/1–2		mm	47/58	16	11	20	27	25	14/27.5	23
0.7–1/0.5–1		mm	25/31	13	7	12	41	38.5	10/37	41
0.5–0.7/0.25–0.5		mm	6/7	10.5	5	9	19	19	9/21	21
0.25–0.5/0.1–0.25		mm	2/3	14	4.5	9	9	11	12/11	11
< 0.25/< 0.1		mm	0.6/0.7	12	3	6	4	6	11/3	3

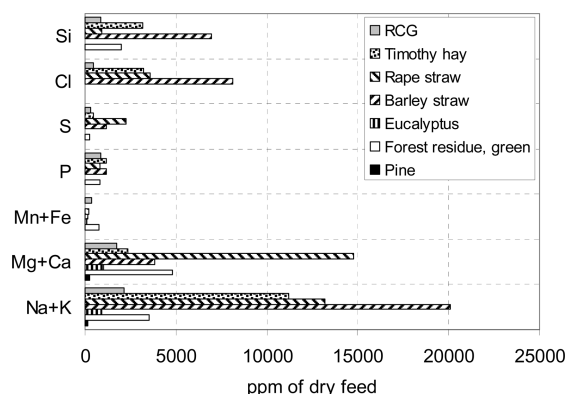


Figure 4. The content of different elements in dry feedstock.

mixes and stump wood from clear cuts and wood chips from forest thinnings), and eucalyptus. The fresh/green forest residue composed of approximately 86% spruce, 9% pine, and 5 wt % birch. The share of needles, based on the content of extractives, was estimated to be 25 wt %. The stored/brown forest residue was composed of 80% spruce, 10% pine, and 10 wt % birch, and the share of needles was estimated to be 7 wt %. Eucalyptus (*Eucalyptus Grandis*) was shipped from Brazil as fresh logs, which were moistened with water during the transport. In Finland, the logs were peeled and the stems were chipped (moisture content 40 wt %), and dried (at 40 °C to a moisture content of 7 wt %). All wood fuels were ground to particle size less than 3–5 mm.

Agricultural residues used were straws from barley and rapeseed, timothy hay (a typical fodder hay in Finland), and reed canary grass (RCG, an energy grass). They were pelletized before grinding to avoid potential feeding problems. The baled straws and grasses were cut to obtain particle size below 6 mm. The cuttings were pelletized, crushed, and sieved to 3–5 mm particle size fraction for PDU (20 kg/h) and below 2 mm for bench scale pyrolysis unit (1 kg/h).

Fuel Analyses. Fuel analyses (Table 1) were carried out using standard methods. The elementary composition (Figure 4) of ash (ashing at 500 °C to avoid losses of alkali metals) was analyzed by Philips PW2404 X-ray spectrometer connected to semiquantitative SemiQ program. The detection limit for the elements was about 0.01%, except for fluorine (0.2 wt %).

Chemical Composition of Biomasses. Chemical composition (Figure 5) of feedstocks were carried out by total hydrolysis

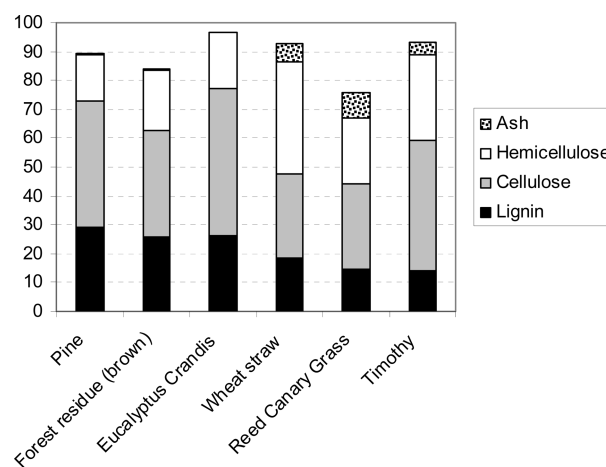


Figure 5. Chemical composition of feedstocks for pyrolysis experiments.

at vTI (Hamburg, Germany), and at University of Jyväskylä (Jyväskylä, Finland). In acid hydrolysis of biomass feedstocks, 5–17 wt % of the material could not be identified. The unidentified fraction consists primarily of extractives.

Liquid Production. The process development unit (PDU) of VTT employs a transport bed reactor (Figure 6). The feedstock is fed to the reactor by a screw feeder. Pyrolysis temperature is about 480–520 °C, and the residence time for pyrolysis vapors about 0.5–2 s. The main part of the char particles as well as heat transfer sand is removed by cyclones from a hot stream of product gases and vapors before entering to liquid scrubbers. The product vapors are condensed in liquid scrubbers, where the product liquid is used as a cooling agent. The amount of raw material and the amount of product liquid is measured by weighing. Typical product yields from pine wood are 64 wt % organic liquids, 12 wt % product water (chemically dissolved in organic liquids), 12 wt % char, and 12 wt % noncondensable gases. Separation of the top phase from the pine/forest residue product liquid is done at 35 °C within 24 h by the standard method described earlier.²⁵

(25) Oasmaa, A.; Kuoppala, E.; Gust, S.; Solantausta, Y. *Energy Fuels* 2003, 17 (1), 1–12.

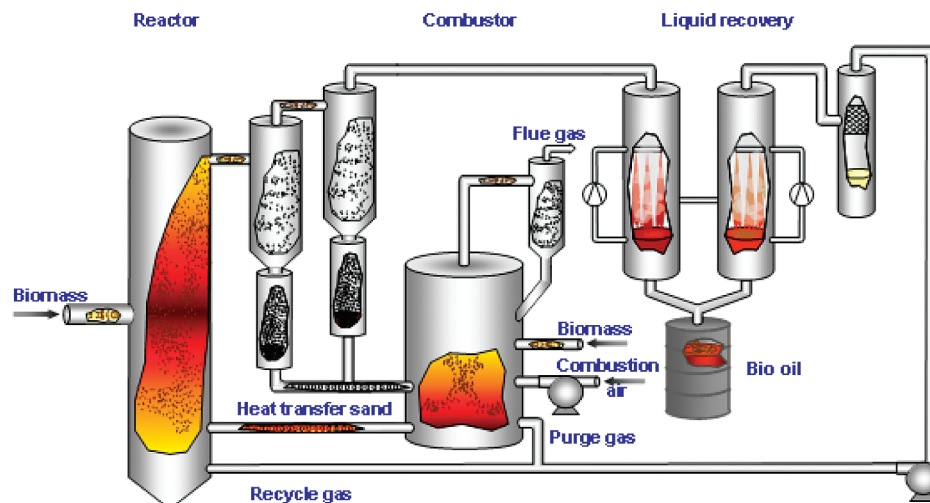


Figure 6. VTT PDU (20 kg/h) pyrolysis unit.

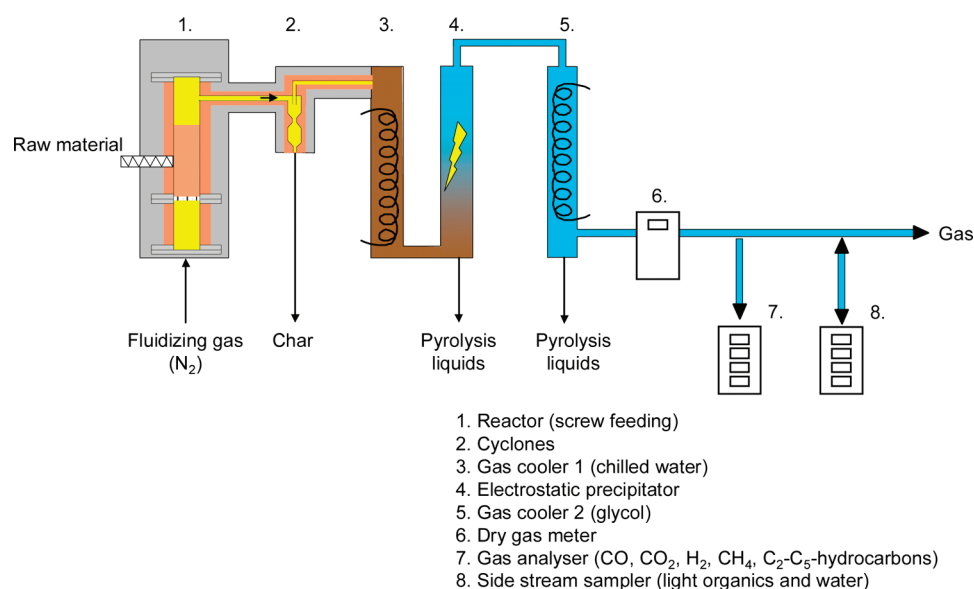


Figure 7. Schematic flow diagram of the bench scale fast pyrolysis unit.

The 1 kg/h bench scale unit (Figure 7) is based on a bubbling fluidized-bed reactor. Aluminum oxide sand is used as fluidizing agent. The pyrolysis temperature is between 440 and 520 °C. The gas phase residence time is typically 0.6–0.7 s. The particle size of raw material is below 2 mm, and moisture content is typically below 10 wt %.

The main part of the char particles in hot product gas/vapor stream is separated by cyclones. After that, gases and vapors are cooled first indirectly with water in a stainless steel condenser. Tar fog (aerosols) is recovered with an electrostatic precipitator. Gases and vapors are then led to the second cooler and cooled indirectly with glycol (−20 °C). The main part of the condensed liquids is recovered from the electrostatic precipitator and the rest, consisting mainly water and light organics, from the second glass cooler. The amount of light organic vapors and water vapor passing the glycol cooler is condensed in a side stream sampler where the gas flows through glass wool bundles and cools down to −50 to −60 °C. The amount of water is determined directly from the main sample liquids by Karl Fisher titration method. The amount of raw material and the amount of product liquids is measured by weighing. Total amount of liquids (organic liquids and water) at the walls is determined as difference by weighing. The small amount of water in the wall

liquids liquids or in glass wool liquids is determined by Karl Fisher titration method from methanol washings.

Liquid Analyses. Physical characterization of pyrolysis liquids is carried out at VTT by employing modified standard and new methods.²⁶ Chemical characterization was performed using the solvent extraction scheme²⁷ based on water extraction. In this method, the following water-soluble (WS) fractions were obtained: carboxylic acids, ether-solubles (mainly aldehydes, ketones, and lignin monomers), water, and ether-insolubles, sugar-type compounds (mainly anhydrosugars, anhydrooligomers, hydroxy acids carrying less than 10 carbon atoms). The water-insoluble (WIS) fraction consisted of dichloromethane-soluble (low-molecular-mass LMM lignin material, extractives) and dichloromethane-insoluble (high-molecular-mass HMM lignin material, solids) substances. Of volatile acids, the main compounds, acetic, formic, and glycolic acids (about 95% of volatile acids) were quantified by using capillary electrophoresis equipment.

(26) Oasmaa, A.; Peacocke, C. *A Guide to Physical Property Characterisation of Biomass-Derived Fast Pyrolysis Liquids*, VTT Publication 450; VTT: Espoo, Finland, 2001; 65 pp + app. (34 pp).

(27) Oasmaa, A.; Kuoppala, E.; Solantausta, Y. *Energy Fuels* 2003, 17 (2), 433–443.

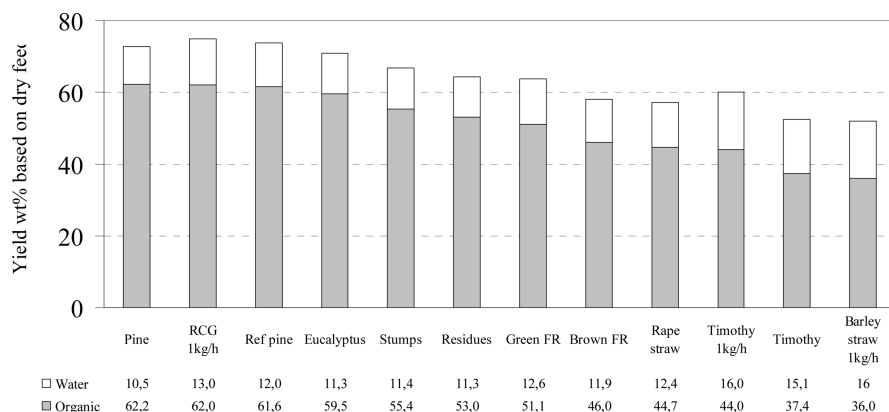


Figure 8. Liquid yields from pyrolysis of wood and grasses in 20 and 1 kg/h units (1 kg/h runs marked). RCG = reed canary grass. FR = forestry residue. Residues = forest thinnings.

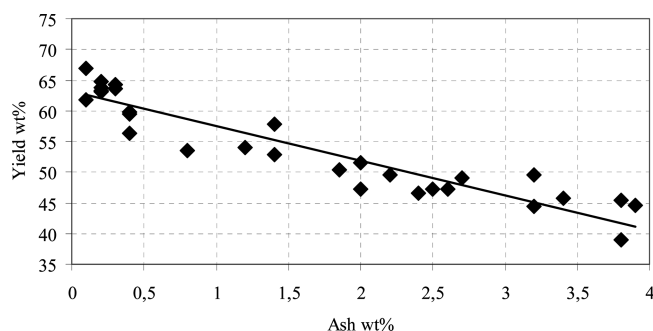


Figure 9. Correlation of feedstock ash to the organics yield in pyrolysis of biomass.

Gas Analyses. The main gaseous products (CO , CO_2 , and CH_4) in pyrolysis gases were determined with a continuous gas analyzer based on a near-infrared method (NIR). The meter was also equipped with an oxygen gas detector based on the use of a zirconium oxide cell. The detailed gas analysis (H_2 , CO , CO_2 , CH_4 , and C_2 – C_5 hydrocarbons) is made using gas sample bottles and gas chromatographs equipped with thermal conductivity (TC) and flame ionization detectors (FID).

Results and Discussion

Feedstock Composition. Agricultural residues contained less lignin and more hemicelluloses (Figure 5) and ash/alkali metals (Table 3) than wood biomasses. Hence, their O/C molar ratio was higher (0.91–1.05) than for softwoods (0.82–0.85).

The ash content of RCG was low (1.1 wt %), possibly due to the soil type and weather conditions. Normal ash content for spring-harvested RCG in Finland is 3–7.5 wt %. The amount of alkali (Na, K) and earth alkali (Mg, Ca) metals were highest with agricultural residues (except RCG) ranging from 14 000 (timothy) to 28 000 (rape straw) ppm and were lowest with wood biomasses (below 4000 ppm). The silicon content was highest (about 7000 ppm) with barley straw and lowest (about 900 ppm) with RCG. The low silicon (Si) content of RCG reflects low amount of dissolved silica in uptake water of RCG, which is typical for sandy soils.²⁸

The chlorine content of wood biomasses is lower (< 0.05 wt %) than that (> 0.5 wt %) of straws and grasses. The higher

chlorine and potassium content for autumn harvested crops (barley straw, rapeseed straw, and timothy hay) and the lower chlorine and potassium content for the spring harvested crop (reed canary grass) are quite typical.

Product Yields. Organic liquid yields were highest for wood biomass and lowest with agro-biomass containing a high amount of alkali metals. Alkali metals also caused yields of product water and gas to be higher for agro-biomass than for wood biomass. The highest organic liquid yields (62 wt %) were obtained with pine saw dust and were lowest (36–45 wt %) with straws and hay (Figure 8). Organic liquid yield for forest fuels was 46–55 wt %. Organic yield from RCG was high (62 wt %) but may not be representative for this material.

Ash content correlated to liquid yields (Figure 9). Alkali metals, mainly potassium, are known to catalyze pyrolysis reactions to yield extra water and gas and decrease the organic liquid yields of agricultural residues.²⁹ Process temperature has been varied between 480 and 520 °C in this data. In case the liquid contains an unusual high amount of silica, the correlation versus ash is not valid and should be drawn versus alkali metals (or Na + K).

The amount of volatiles (Figure 10) correlated also with organic yields as well as feedstock O/C molar ratio (Figure 11).

The organic liquid yields as well as the liquid quality for pine wood from the PDU and bench-scale units were practically the same (Table 2). With agro-biomass (timothy hay) the results differed. Higher organic liquid yield for Timothy hay was obtained in the 1 kg/h than in the 20 kg/h unit. Accumulation of alkali metals into the recycle sand and its catalytic effect to thermal decomposition reactions could also be a reason for smaller organic liquid yield of the PDU experiment. The composition of product liquids was quite similar.

Top Phase Formation. A separate top phase was formed with feedstocks having a high amount of extractives (neutral substances), for example, forestry residues and pine.²⁵ Bark produces an even larger top phase.³⁰ The bottom phase dissolved only a certain amount (3–5 wt %) of extractives. The amount of top phase varied from 1 to 20 wt % depending mainly on content of extractives in feedstock. Pine produced smaller top phase than forest residue. The amount of top phase can be decreased by keeping the condensed liquid for a while (about 9 h) at elevated temperature (about 35 °C) where

(28) Bakker, R. B.; Elbersen, H. W., Managing ash content and quality of in herbaceous biomass: an analysis from plant to product. 14th European Biomass Conference, Paris, France, Oct. 17–21, 2005; pp 210–213.

(29) Coulson, M., Pyrolysis of perennial grasses from southern Europe. *Thermalnet Newsletter* **2006**, 2, 6–7.

(30) García-Pérez, M.; Chaala, A.; Pakdel, H.; Kretschmer, D.; Rodrigue, D.; Roy, C. *Energy Fuels* **2006**, 20, 364–375.

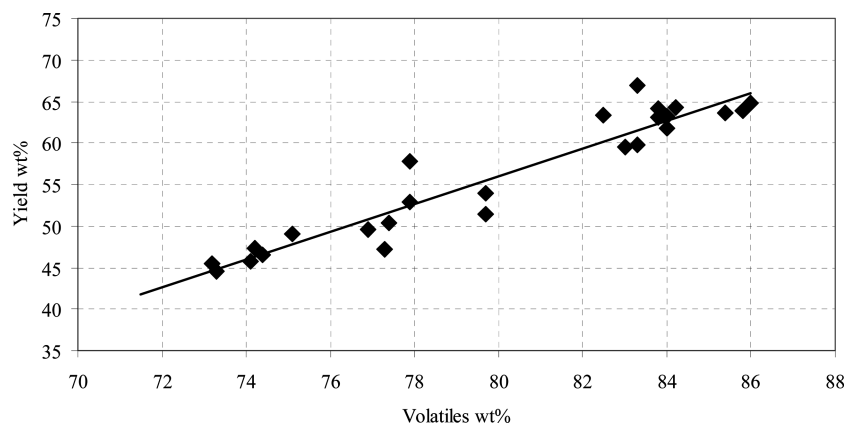


Figure 10. Yield of organic liquids in biomass pyrolysis as a function of feedstock volatile matter, wt % based on dry feed.

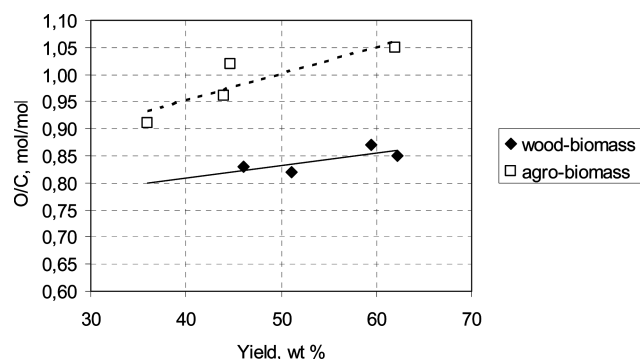


Figure 11. Yield of organic liquids (wt % based on dry feed) in biomass pyrolysis as a function of feedstock O/C ratio.

Table 2. Comparison of the Properties of Pine Sawdust Liquids from 1 kg/h (525 °C) and 20 kg/h units (520 °C)

pyrolyzer		1 KG/H			
expt. No.	PDU 20 KG/H	1a	1b	1c	1d
feedstock moisture (wt %)	4.5	4.0	4.0	4.4	4.4
liquid yield (wt % dm)	74	74	74	71	71
recovery percentage (wt %)		93	91	91	92
water (wt %)	17.0	17.6	17.8	15.9	15.9
pH	2.4	2.4	2.4	ND	ND
density (15 °C) (kg/dm ³)	1.2	ND	1.24	1.25	1.25
viscosity (50 °C) (cSt)	27.5	ND	23	28	28
HHV (MJ/kg)	18.7	18.2	18.3	18.9	18.8
LHV (MJ/kg)	17.2	16.7	16.8	17.2	17.3
carbon (wt % dm)	45.7	45.0	44.8	46.2	46.2
hydrogen (wt % dm)	7.0	7.0	7.0	7.0	7.0
nitrogen (wt % dm)	<0.1	<0.1	<0.1	<0.1	<0.1

most of extractives are in liquid form.²⁵ Addition of alcohol reduces³¹ the amount of top phase (open squares in Figure 12).

Liquid Quality. Wood pyrolysis liquids as well as liquid from RCG were homogeneous, containing 21–27 wt % water. Other liquid products from agricultural residues were nonhomogenous, having high (39–51 wt %) water contents. High alkali content of feedstock increased water production and yielded high water content in product liquid. Most water was produced with timothy hay and barley straw, which have the highest alkali contents. Water content of product liquid correlates with physical properties such as density, viscosity, and heating value.²⁶

(31) Oasmaa, A.; Kuoppala, E.; Selin, J.-F.; Gust, S.; Solantausta, Y. *Energy Fuels* **2004**, *18* (5), 1578–1583.



Figure 12. Correlation of the amount of top phase with the extractive content of the product liquid. Solid squares with no alcohol addition, open squares with 5 wt % alcohol addition. Addition of alcohol diminished the amount of top phase.

Content of nitrogen was low (≤ 0.1 wt %) in liquids from pine and eucalyptus. Nitrogen content was higher in liquids (forest residues) containing bark or needles, which are high in N. Liquids from agricultural residues contained 0.5–1 wt % N. Similar trend was measured for sulphur. The lowest S content (0.01 wt %) was with pine and highest (0.05 wt %) was with agricultural residues. The chlorine content is < 0.01 wt % for pine liquids, but as high as 0.5–0.8 wt % for liquids from agricultural residues. Liquids from agro biomass may cause corrosion in combustion if the level of Cl cannot be controlled. High levels of N and S also have to be controlled. The pH of straw and grass liquids was higher than that for wood liquids, possibly due to a lower amount of formic acid, as well as higher amount of water. Other reasons may be the higher level of nitrogen being in the form of basic nitrogen compounds. Also, the pH of the straw and grass pyrolysis liquids may be dependent on the alkali content of the liquids.

The heating value (dry basis) is a little lower for agro biomass than for wood biomass due to lower amount of lignin in agricultural residues. High water content of agro biomass liquids decreases LHV to a low level considering combustion.

Chemical compositions of product liquids obtained with the solvent fractionation method are shown in Figure 13. Volatile acids are shown in Table 4. Figure 14 shows the change in chemical composition of feedstock organic matter during pyrolysis.

The comparison of the chemical composition of feedstock and liquid products shows that feedstock lignin is thermally

Table 3. Fuel Oil Properties of Pyrolysis Liquids from Wood, Straw, and Grasses^a

feedstock bio-oil	pine <i>P. Syl.</i>	FR brown	FR green	eucalyptus <i>Crandis</i>	barley straw	timothy hay	RCG
water (wt %)	23.9	26.7	25.5	20.6	51.1	39.3	27.4
solids (wt %)	0.01	0.17	0.09	0.09	0.43	0.01	0.15
ash ^b (775 °C) (wt %)	0.03	0.3	0.1	0.03	ND	0.004	ND
carbon (wt %)	40.6	41.4	41.2	42.3	26.5	32.1	39.3
hydrogen (wt %)	7.6	7.4	8.0	7.5	9.0	8.5	7.7
nitrogen (wt %)	< 0.1	0.3	0.3	0.1	0.9	0.6	0.6
sulfur (wt %)	0.01	0.03	0.02	0.02	ND	ND	ND
chlorine (wt %)	0.006	0.002	0.004	ND	ND	ND	ND
oxygen (diff.) (wt %)	51.7	50.9	50.5	50.1	62.7	58.7	51.8
Na (ppm)	< 5	ND	8	ND	ND	ND	ND
K (ppm)	34	110	89	ND	ND	ND	ND
viscosity (40 °C) (cSt)	17	17	24	23	ND	5	ND
density (15 °C) (kg/dm ³)	1.206	1.194	1.210	1.229	ND	1.150	ND
flash point (°C)	53	42	65	101	ND	ND	ND
pour point (°C)	−36	−12	−27	−42	ND	ND	ND
HHV (MJ/kg)	16.9	16.9	16.7	17.3	11.1	13.3	16.0
LHV (MJ/kg)	15.3	15.3	15.2	15.6	9.1	11.5	14.3
LHV (dry basis) (MJ/kg)	20.1	20.9	20.4	19.7	18.6	18.4	19.7
pH	2.7	3.2	ND	2.2	3.7	3.4	3.6

^a Some uncertainty may be in results for pyrolysis liquids from straw and hay because of unhomogeneity of these liquids. ^b Ash and solids may not be in line. Ash forming constituents have not been characterized. FR = forest residue, RCG = reed canary grass, ND = not determined

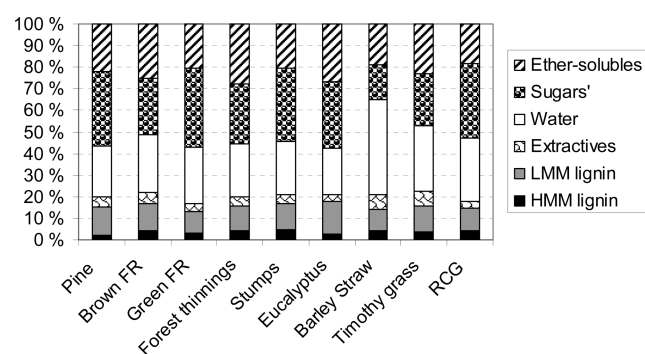


Figure 13. Chemical composition²⁷ of product liquids from pyrolysis of woods fuels (pine, forest residues, eucalyptus), and agricultural residues (barley straw, timothy hay, reed canary grass). The fractions are described in the Experimental section.

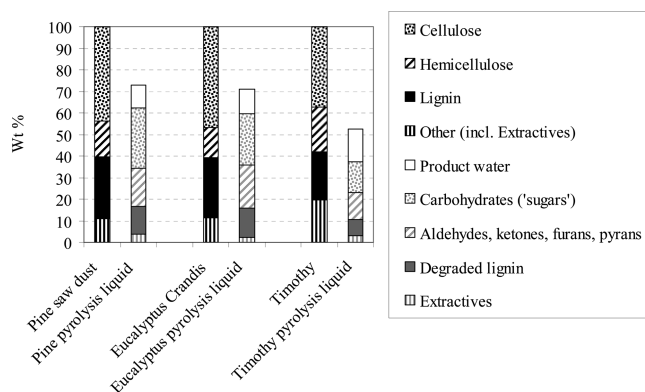


Figure 14. Organics in feedstocks and liquid products (wt % dm). Feedstock moisture excluded.

cracked more with agro biomass than with wood. Alkali metals present in large amounts in agro biomass may also catalyze thermal cracking of lignin. The ratio of cellulose/(sugars and product water) is similar, 1.0–1.3, in all experiments, which suggests that cellulose degrades basically into mix of sugars and water. Hemicelluloses degrade mainly into acids and gases, which is seen in the amount of volatile acids (Table 4) in liquid and in gas composition (Table 6). The CO/CO₂ (Table 5) ratio was 0.4–0.6 with grasses and straw,

whereas it was 1 with wood. Grasses and straw contain more hemicellulose than wood, hence more CO₂ is formed.

The product liquid of RCG obtained from the bench scale pyrolysis unit was of good quality. Water content of a single-phase liquid was 27 wt %, and the liquid was homogeneous. Straws contained the highest amounts of ash and yielded a separate aqueous and heavy lignin phase.

The GC-eluted compounds in grass and straw liquids were similar. Product liquid from timothy hay contained a lot of small ether-soluble compounds, like furans, which kept product liquid as a single phase despite high water content. Product liquid of barley straw was nonhomogeneous and had a water content above 40 wt %. High ash/alkali content of the barley straw caused a high level of chemical water formation, because also sugars had decomposed.

Composition of extractives differ between grasses and wood, as do the extractives in product liquids. Main compounds of grass extractives are fatty acids when softwoods also contain a lot of resin acids. Grass lignin is both guaiacyl and syringyl type and softwood lignin guaiacyl type.

Economic Performance of Integrated Pyrolysis. It has been suggested previously that integration of a pyrolysis reactor to a combined-heat-and-power (CHP) boiler will bring both operational and economic advantages. In the following example, economic advantages of the concept (Figure 3) is presented, when pyrolysis is integrated to a state-of-the-art fluidized-bed boiler. Three bio-oil production cases are compared using sawdust, forest residue, and straw as fuel to a pyrolyser. Only fixed costs and income from power, heat, and bio-oil are considered, that is, variable and capital costs are not taken into account. However, this is considered adequate to highlight the difference between stand-alone and integrated pyrolysis, as both variable and capital costs for all cases will be fairly similar.

In all cases use of a same fuel for the main boiler is assumed. The bases for the calculation are presented in Table 6 and below. Net heat production in the boiler is calculated from gross heat production by subtracting heat demand for drying of pyrolysis fuel feed. Heat is therefore provided in the calculation with primary heat, which is a simplification, but adequate for the purposes of this example.

The integrated concept suits especially well to bio materials, which have a lower organic liquid yield than sawdust

Table 4. Volatile Acids of Pyrolysis Liquids

feedstock	pine, <i>Pinus sylvestris</i>	eucalyptus, <i>Grandis</i>	barley straw	timothy hay 1 kg/h	timothy hay 20 kg/h	reed canary grass
acetic acid (wt %)	2.2	4.7	3.2	4.5	4.9	3.8
formic acid (wt %)	1.2	1.2	0.3	0.5	0.8	1.0
glycolic acid (wt %)	0.4	0.4	0.1	0.1	0.3	0.3
total (wt %)	3.8	6.3	3.6	5.1	6.0	5.2

Table 5. Yield of Carbon Monoxide and Carbon Dioxide in Bench Scale Experiments (wt % of dry feed)

feedstock	pine	barley straw	rapeseed straw	timothy hay	RCG
CO (wt %)	5.7	5.0	3.8	5.3	3.5
CO ₂ (wt %)	5.2	11.8	11.5	11.3	5.7
CO/CO ₂	1.1	0.4	0.3	0.5	0.6

Table 6. Bases for the Performance Evaluation

CHP-boiler capacity (MW thermal)	40
power production (MW electrical)	12
gross heat production (MW thermal)	24
boiler fuel moisture (wt %)	50
pyrolysis fuel feed (MW thermal)	20
initial pyrolysis feed moisture (wt %)	
-both wood	50
-straw	30
moisture to pyrolysis reactor (wt %)	8
bio-oil production (MW thermal)	
-sawdust feed	14.0
-forest residue feed	11.5
-straw feed	8.6
net heat production (MW thermal)	
-wood fuels	20.4
-straw fuel	22.7

Table 7. Basis for the Economic Assessment of the Concept

fuel cost (euro/MW thermal)	14
value of electricity (euro/MW electrical)	30
value of heat (euro/MW thermal)	15
value of bio-oil (euro/MW thermal)	30
annual operation time (h/a)	5000

Table 8. Performance Figures for Pyrolysis Including Boiler Fuel Demand

	pyrolysis feed (MW thermal)	bio-oil (MW thermal)	bio-oil (kg/s)	char (MW thermal)	gas (MW thermal)	heat for pyrolysis (MW thermal)	boiler fuel (MW thermal)
sawdust	20.4	14.0	0.9	5.1	0.9	3.0	37.1
forest residue	20.4	11.4	0.8	8.2	0.9	2.7	33.6
straw	20.4	8.6	0.7	10.1	1.2	2.5	31.2

(Figure 8). This due to the fact that for a fixed pyrolysis feed, increased char and gas production (as in the case of forest residue and straw) will be replacing boiler fuel reducing boiler fuel cost. Performance figures for bio-oil production, boiler fuel, and pyrolysis byproduct are given in Table 8. It is seen that although production of bio-oil is considerably reduced when straw is used as feed compared to sawdust, demand for boiler fuel is also reduced.

The economic aspects of integration are summarized in Table 9 below. Only fixed costs and income from power, heat, and bio-oil are considered. Production of electricity and heat are the same for wood fuels, whereas heat production is slightly more for the straw case due to a reduced drying demand. It is seen that compared to the income from bio-oil from sawdust, income from forest residue and straw bio-oil are reduced 18 and 39%, respectively. When overall expenses are deducted from income it may be seen, again using the sawdust case as the reference, that these differences from forest residue and straw bio-oil are reduced only 10

Table 9. Income and Expenses in Integrated Production, Million Euros

	sawdust	forest residue	straw
Income			
electricity	1.8	1.8	1.8
heat	1.5	1.5	1.7
bio-oil	2.1	1.7	1.3
sum	5.4	5.1	4.8
oil income %	100	82	61
Expenses			
boiler fuel	2.6	2.3	2.2
pyrolysis fuel	1.4	1.4	1.4
sum	4.0	3.8	3.6
income – expenses	1.4	1.3	1.2
difference %	100	90	83

and 17%, respectively. This is clear evidence of the competitiveness of the integrated concept. When a pyrolyser is operated in a stand-alone mode, there will always be a challenge of using the byproduct in an optimal manner. In the case of the integrated concept there is not such a problem.

Conclusions

The highest organic liquid yields and lowest product water and gas yields were obtained with wood feedstocks. Agricultural residues produced the lowest organic liquid yields mainly due to presence of high amounts of alkali metals catalyzing cracking reactions. A rough indication of expected organic liquid yields can be obtained by analyzing the volatile, ash/alkali content, or O/C molar ratio of the feedstock to be pyrolyzed. All of these properties correlate well with the organic liquid yield.

The feedstock lignin was thermally cracked more with agro biomass than with wood. This may be because of high amount of alkali metals in agro biomass catalyzing thermal cracking of lignin. Cellulose degraded basically into a mix of sugars and water, and there was no clear difference between the feedstocks. Hemicelluloses degraded mainly into acids and gases. Grasses and straw contain more hemicellulose than wood, so gas formation was larger with agro biomasses. Also, more CO₂ was formed with agro biomasses.

The quality of pyrolysis liquids was typically good, when the water content of the product liquid was below 30 wt % and the solids content was below 0.5 wt %. Nitrogen, sulfur, and chlorine contents were higher with agro biomasses and forest residues than with bark-free wood (pine sawdust, eucalyptus).

The integrated concept suits especially well to bio materials, which have a lower organic liquid yield than sawdust. The competitiveness of the concept is verified.

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