

Production of bio-oil from forest residue

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Abstract

Fast pyrolysis is a thermal decomposition process, which occurs in the absence of oxygen, to convert biomass into a liquid product. Forest residue has been considered as the most important raw material for fast pyrolysis in Finland. The bio-oil produced during fast pyrolysis is very dependent on the feedstock and the process conditions. In this paper the forest residue quality and the composition of bio-oil are discussed.

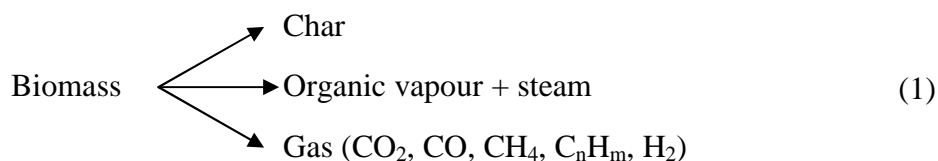
Introduction

Biomass is a renewable raw material which can be used for heat and fuel production. Solid biomass properties can be improved for example by pelletization, but converting them to liquid may further expand their utilization. Liquid bio fuels are easier to store, transport and handle than solid biomass. [1] Fast pyrolysis is a promising process to produce liquid fuels from biomass. During fast pyrolysis the biomass is heated very quickly up to around 500 °C in the absence of oxygen. After pyrolysis the vapours are cooled down rapidly to give a dark brown fluid liquid called bio-oil or pyrolysis liquid. The bio-oil is immiscible in fossil fuels and it has a heating value of about half of what a conventional fuel oil has. For traffic fuels bio-oil can not be used without upgrading. [2]

Many different types of biomass can be used as a raw material in fast pyrolysis. In Finland forest residue is besides sawdust, one of the most feasible feedstock for liquid fuel production. Compared to bark free wood, forest residue contains a lot of extractives and ash due to the presence of needles and bark, which affect the quality of the bio-oil. [1]

Fast pyrolysis

Fast pyrolysis is the thermal decomposition of biomass in the absence of oxygen. Pyrolysis is always the first stage in combustion and gasification followed by total or partial oxidation. In gasification a fuel gas is mainly produced, while in pyrolysis pyrolysis liquid, char and gas are the main products (equation 1). [2, 3, 4, 5]



The yield of the liquid product is very dependent on the temperature, heating rate and residence time of the raw material. Lower process temperatures (400 °C) and longer vapour residence times (20 s) favours the production of char while higher temperatures (800 °C) and longer vapour residence times favours the gas formation. [4] The highest liquid yield is obtained with fast or flash pyrolysis, where the biomass is heated up very fast (1000 °C/s) to a moderate temperature (500 °C) during very short vapour residence time (<2 s). In this case the organic liquid yield can be up to 65 wt- % for sawdust. [11] For forest residue the liquid yield is lower (50 wt- % for brown forest residue and 55 wt- % for green forest residue). [1] The most difficult

stage in fast pyrolysis is to heat up the biomass particle to the optimum temperature, so that its exposure at lower temperature is as short as possible. One way to overcome the problem is to grind the biomass before pyrolysis. The particle size of the biomass used in the fluidized bed demonstration plants (figure 1) is usually 2-6 mm.

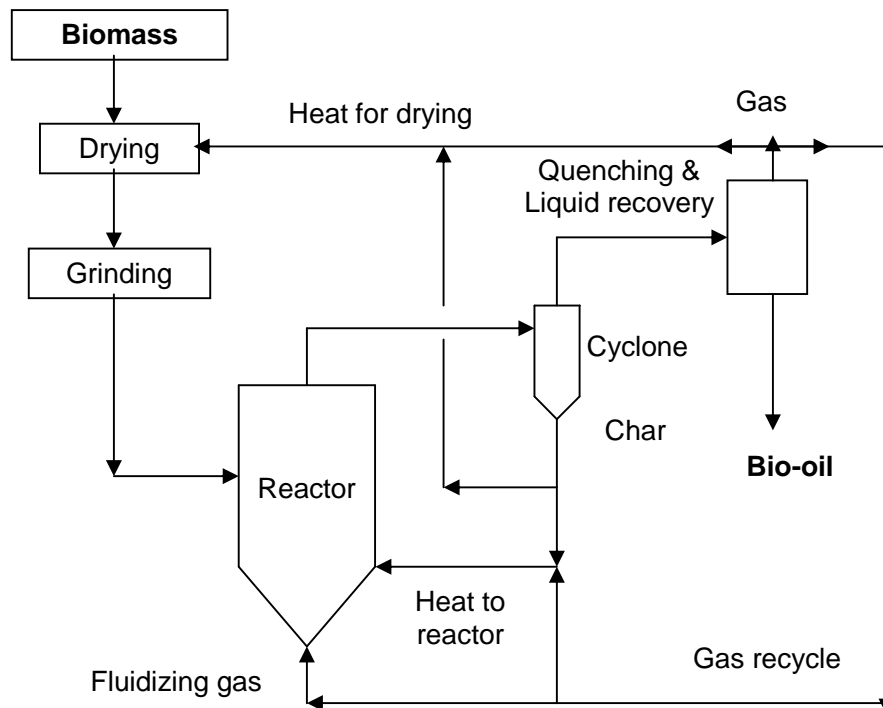


Figure 1. Principle of a fast pyrolysis process [2].

In addition to grinding, the raw material is usually also dried to a moisture content below 10 wt- %. By grinding and drying the raw material, the liquid yields will increase, but at the same time also the production costs of the pyrolysis liquid will increase. [2, 3, 4]

After drying and grinding, the biomass is fed into the pyrolysis reactor. For fast pyrolysis a wide range of different reactor configurations have been investigated. The most important reactor types are bubbling fluidized bed, circulating fluidized bed, rotating cone, ablative and entrained flow reactor. [2, 3, 4] For commercial operation so far only circulated fluidized bed reactor has been used for food flavouring production [2].

The char, formed during pyrolysis, acts as a vapour cracking catalyst and should therefore be separated from the gases immediately after pyrolysis. For char removal cyclones are usually used. However, some small char particles always pass through the cyclones and are mixed with the liquid product. For char removal hot vapour filtration has been tested. [2, 3, 4]

After solid separation the vapours and the gases must be quenched rapidly to avoid continuous cracking of the organic molecules. Quenching of the vapours is usually done with pyrolysis liquid condensers, where the vapours are cooled directly with the bio-oil or a hydrocarbon liquid. Part of vapours are as aerosols, which are very difficult to condense with normal tray and package towers. Therefore electrostatic precipitators are also used to capture the aerosols. [2, 3, 4]

Forest residue as a feedstock in fast pyrolysis

Wood is the most important raw material for fast pyrolysis in Finland [1]. The main user of wood is the forest industry, but from end cuttings remains a lot of logging residue, which can not be exploited in the forest industry. This forest residue is currently collected as boiler fuel, but may also be used for fast pyrolysis. [6]

The chemical composition of forest residue is very dependent on the species of wood and the amount of branches, tree tops, stumps, and the extent of decay. In, for example, wood needles and bark, the amount of extractives are significantly higher than in bark free wood (table 1). Also the ash content is higher in needles and bark than in bark free wood. [7]

Table 1. Composition of softwood, forest residue, needles and bark [7].

	unit	pine stem wood	brown forest residue	green forest residue	spruce needles	spruce bark
ash, d.m	wt- %	0,2	3,8	2,1	6,65	2,3
carbon, d.m.	wt- %	50,3	51,1	51,4	48,4	49,9
hydrogen, d.m.	wt- %	6,0	5,9	6,0	6,1	5,9
nitrogen, d.m.	wt- %	<0,1	0,5	0,5	0,6	0,4
oxygen, d.m.	wt- %	43,5	38,7	40,0	38,3	41,4
extractives, d.m.	wt- %	5,9	5,4	10,5	20,3	21-24

In Finland the majority of forest residue compose of spruce and pine from end cuttings. Forest residue can be logged either as green (moisture about 55 wt- %) with needles or as brown after seasoning (moisture about 35 wt- %) when around half of the needles and a small amount of thin branches remain in logging area. Green residue of spruce contains 40 % of wood, 23 % of bark and 37 % of needles on average. The corresponding numbers for brown residue are over 60 % of wood below 30 % of bark and below 10 % of needles. During storage the amounts of extractives will decrease due to the loss of bark and needles but also due to the hydrolysis of triglycerides, oxidation of resin acids and evaporation of volatile terpenes. The loss of bark and needles also slightly decrease the amount of ash in brown forest residue, but on the other hand sand and other inorganic compounds from the soil increase the total ash content in brown forest residue. Low ash content is feasible in fast pyrolysis, because the ash catalyses the vapour cracking, which decrease the liquid yield. [7]

Composition of bio-oil from forest residue

The composition of bio-oil recovered from forest residue differs a lot from bark free wood. Forest residue liquid separates directly after condensation to a polar liquid bottom phase and a hydrophobic viscous top phase. The amount of top phase is usually 10-20 wt- % depending on the feedstock. [7]

The bottom phase is similar to bio-oil recovered from bark free wood. The bottom phase contains 75-80 wt- % water-soluble material and 20-25 wt-% of water insoluble material (figure 2). [7]

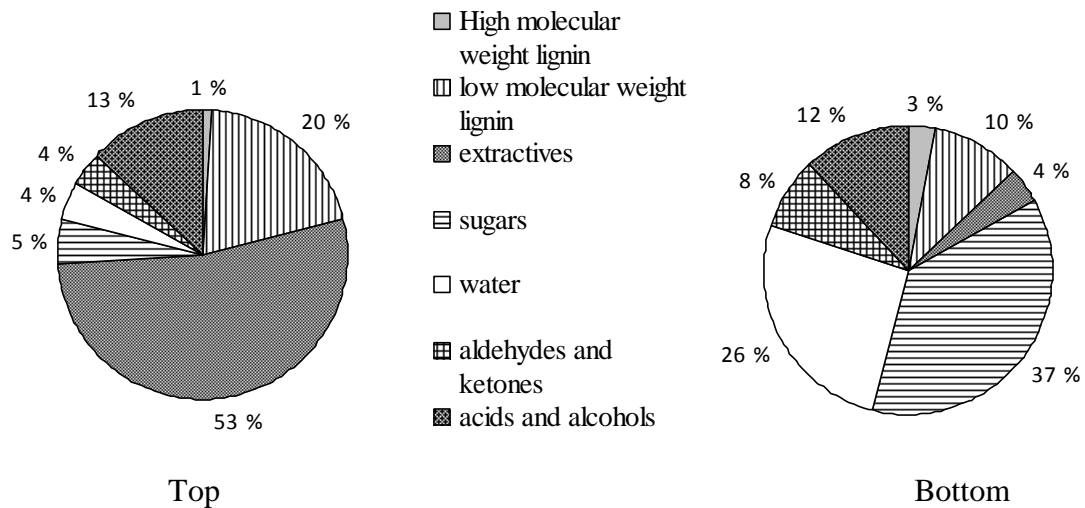


Figure 2. Chemical composition of bottom and top phase in green forest residue liquid [7].

The top phase differs significantly from the bark free wood due to the high amount of extractives. In good phase separation the water soluble fraction is less than 30 wt- % and the amount of extractives bigger than 50 wt- % in the top phase. [8]

There are also some small differences in the chemical composition of bio-oil recovered from brown and green forest residue. Green forest residue produces usually more extractives and sugars than brown forest residue. [8]

Bio-oil quality

The quality of bio-oil different significantly from the quality of fuels derived from fossil fuels (table 2).

Table 2. Pyrolysis liquid physical properties compared to mineral oil [8].

	unit	green forest residue bottom phase	green forest residue top phase	pine	mineral oil
solids	wt- %	0,07	1,47	0,17	0,01
pH		3,1	3,2	2,5	
viscosity (40°C)	cSt	16	153	35	140-380
density	kg/m ³	1,21	1,11	1,23	0,9-1,02
LHV	MJ/kg	15	26,6	17	40,5
water	wt- %	28,1	10	18,2	<0,7
oxygen	wt- %	52	30	47	1

In contrast to fossil fuels bio-oil contains a large amount of oxygen, usually 45-50 wt- %. The high oxygen content in bio-oil is hold as the primary reason for the differences between hydrocarbon fuels and bio-oil. Due to the high oxygen content, the heating value of bio-oil is 40-45 % of that for fossil fuels and the bio-oil is immiscible in hydrocarbon liquids. [9, 10]

Bio-oil contains also a lot of water, usually 20-30 wt- % depending on the feedstock. The water in the bio-oil comes from the moisture in the feedstock and from the dehydration reaction occurring during pyrolysis. The water content has a negative

impact on the heating value, but on the other hand it improves the bio-oil flow characteristics like viscosity. [9, 10]

Pyrolysis liquid contains also different amounts of organic acids, mostly acetic and formic acids, which result in low pH (2-3). Because of the low pH, bio-oil is corrosive to some common construction materials like carbon steel and aluminium. [9, 10]

Bio-oil has also other disadvantage properties compared to fossil fuels. Bio-oil produced from forest residue is a non homogeneous liquid, because of the phase separation of extractives. The reason for the phase separation of extractives depends on their low oxygen content and their low polarity. Also a high water content (>30 wt- %) in the bio-oil can result in phase separation of the lignin molecules, because the concentration of polar carboxyl and hydroxyl compounds is too low to keep the bio-oil as a micro-emulsion. [7, 10]

The bio-oil contains also compounds that during storage or handling can react with them selves to form larger molecules. This phenomenon, also called aging, results in an increase of viscosity and water content in bio-oil. The aging rate depends exponentially on the temperature of the liquid during storage, but also on the bio-oil composition, pyrolysis conditions, efficiency of solid removal and the liquid recovery system. [10]

Conclusion

Fast pyrolysis is an efficient way to produce liquid fuels from biomass. For fast pyrolysis a wide range of different reactor configurations have been investigated, but still none of them have been used commercially for liquid fuel production.

The quality of bio-oil has to be improved before it can be used as a traffic fuel or combusted in boilers. The quality of the bio-oil can already be improved, before pyrolysis, by changing the harvesting process of forest residue. During the fast pyrolysis process the solid content in the bio-oil can be reduced by efficient char removal.

The phase separation of extractives and the aging of the pyrolysis liquid are very disadvantage properties of a liquid fuel. Alcohol addition has been used to stabilize the bio-oil. During alcohol dilution the density and viscosity of the bio-oil decrease, while the phase separation of extractives increase. To produce a liquid fuel, which is comparable with fossil fuels, the oxygen content and the water content in the bio-oil has to be reduced.

References

1. Solantausta, Y., Oasmaa, A., Fast pyrolysis of forestry residues and sawdust, production and fuel oil quality, *International nordic bioenergy conference* 2003 p. 1 - 3.
2. Bridgwater, A. V., Peacocke, G. V. C., Fast pyrolysis processes for biomass, *Renewable and Sustainable Energy Reviews* 4 (2000) 1 - 73.
3. Bridgwater, A. V., Czernik, S. , Piskorz, J., The status of biomass fast pyrolysis, In *Fast Pyrolysis of Biomass, Volume 2*, CPL Press, Newbur 2002, p. 1 - 19.
4. Bridgwater, T., Biomass pyrolysis, Aston University IEA Bioenergy 2007.

5. Mohan, D., Pittman, C. U., Steele, P. H. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review, *Energy & Fuels* **20** (2006) 848–889.
6. Helynen, S., Flyktman, M., Mäkinen, T., Sipilä, K., Vesterinen, P., Bioenergian mahdollisuudet kasvihuonekaasupäästöjen vähentämisessä, *VTT Research notes*, Edita Prima Oy, Helsinki 2002, p. 9 - 23.
7. 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* **17** (1) (2003).
8. Oasmaa, A., Kuoppala, E., Solantausta, Y., Fast Pyrolysis of Forestry Residue. 2. Physicochemical Composition of Product Liquid, *Energy & Fuels* **17** (2003) 433 – 443
9. Czernik, S., Bridgwater, A., Overview of Applications of Biomass Fast Pyrolysis Oil, *Energy & Fuels*, **18** (2004) 590 - 598.
10. Oasmaa, A., Czernik, S., Fuel Oil Quality of Biomass Pyrolysis Oils-State of the Art of the End Users, *Energy and Fuels* **13** (1999) 914 - 921.
11. Scott, D.S., Piskorz, J., The Flash Pyrolysis of Aspen-Poplar Wood, *Can. J. Chem. Eng.* **60**, 1982, 666-674.