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Recent developments in fast pyrolysis of ligno-cellulosic materials

Sascha Kersten¹ and Manuel Garcia-Perez²

Pyrolysis is a thermochemical process to convert ligno-cellulosic materials into bio-char and pyrolysis oil. This oil can be further upgraded or refined for electricity, transportation fuels and chemicals production. At the time of writing, several demonstration factories are considered worldwide aiming at maturing the technology. Research is focusing on understanding the underlying processes at all relevant scales, ranging from the chemistry of cell wall deconstruction to optimization of pyrolysis factories, in order to produce better quality oils for targeted uses. Among the several bio-oil applications that are currently investigated the production and fermentation of pyrolytic sugars explores the promising interface between thermochemistry and biotechnology.

Addresses

¹Sustainable Process Technology, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, Netherlands

²Biological Systems Engineering, Washington State University, Pullman, WA, USA

Corresponding author: Kersten, Sascha (s.r.a.kersten@utwente.nl)

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Introduction

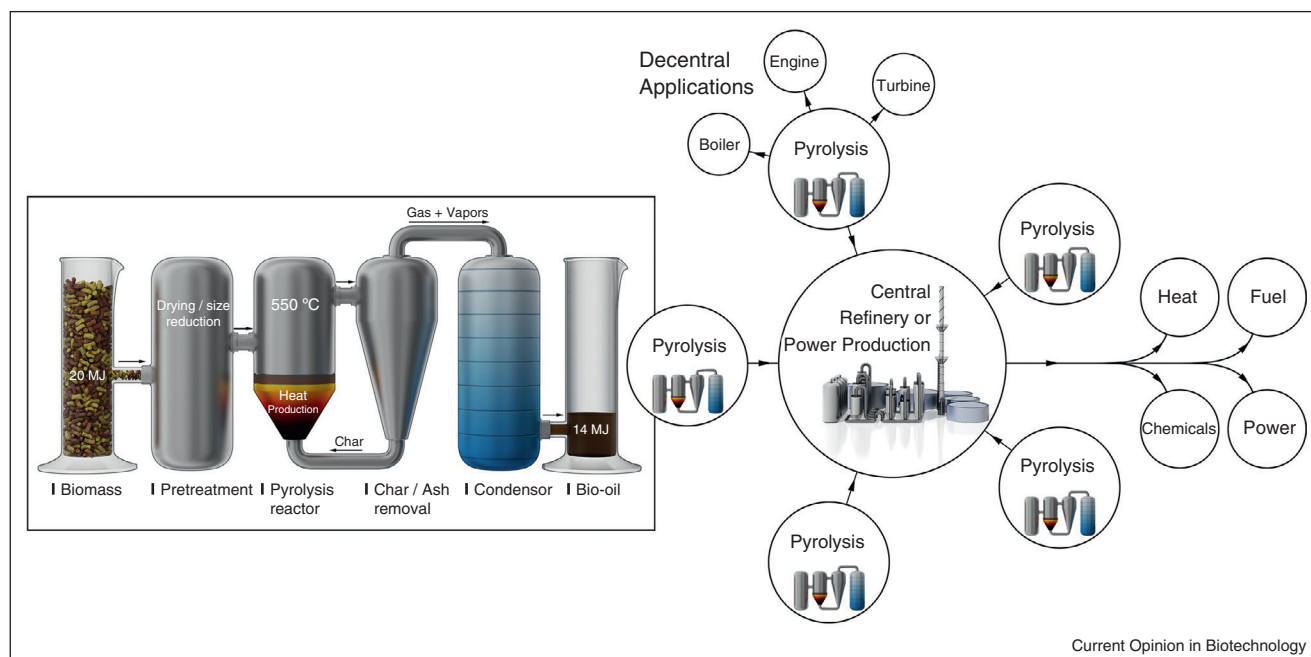
At temperatures between 250 and 550°C in the absence of oxygen biomass particles decompose into char, liquids (removed from the solid as vapors or as aerosols), and gases by a process known as pyrolysis. The liquid product, called pyrolysis oil or bio-oil, is typically condensed and captured downstream of the reactor in single or multistep (staged) condensers. When the pyrolysis is conducted at temperatures between 400 and 550°C and small biomass particles (less than two millimeters) are used, very high heating rates are achieved resulting in maximal liquid production. This process is called fast pyrolysis. Processes conducted at lower temperatures (250–350°C), using larger particles (centimeters), resulting in high char yields are typically known as slow pyrolysis or carbonization. In addition to its practical importance, pyrolysis is also the initial chemical step in all biomass gasification and combustion processes.

Figure 1 shows the pyrolysis process, logistic schemes and proposed oil applications. The advocated advantages of pyrolysis oil are that this liquid can be easily and more economically stored, transported and processed compared to the bulky inhomogeneous solid biomass from which it originates [1,3]. This could enable the uncoupling of biomass production, refining and application locations (see Figure 1) and may be instrumental in returning minerals, via the mineral-rich produced char, to the soil of the biomass production area [2]. Ligno-cellulosic materials such as forest residues (forest thinning, bark), wood processing industries (sawdust) and agricultural residues (straw) and urban wood wastes are the most commonly targeted feedstock for commercial pyrolysis factories [3].

Table 1 shows the typical composition of several crude and upgraded bio-oils. Pyrolysis oil as we know it today is a complex mixture of water and a large variety of oxygenated organic compounds with diverse functional groups (see Table 1; column 1). This liquid may be used as feed for engines, turbines, boilers and gasifiers or can serve as feed for fuels and chemicals production. The latter two applications will require additional refining steps. Oil applications and the bottlenecks hereof are discussed in detail by Czernik and Bridgwater [4]. Some reported adverse properties of pyrolysis oil are its high water content, high oxygen content, high acidity, low heating value and low stability. Obviously, the required pyrolysis oil quality will depend on the application targeted [5^{*}]. Oil improvements can be achieved through actions during, before or after the pyrolysis step. These may include:

1. Demineralizing the feed by an acid wash. This increases the production of fermentable sugars considerably (see Table 1, column 2, 2nd condenser).
2. Application of catalysis within the pyrolysis process. Catalytically active components are added to the biomass particles or heterogeneous catalysts are used to steer reactions of the hot vapors. Catalysis aims at reducing the acidity and oxygen content and increasing the heating value and the production of targeted components (see Table 1; column 5).
3. Staged condensation (two or more condensers in series with decreasing temperature) to lower the acid and water content of the oil (see Table 1; column 2, 1st condenser). The use of staged condensation also results in the production of an aqueous phase rich in small oxygenates such as acetic acid (see Table 1, column 2, 2nd condenser), which can be extracted for fuel or chemicals production.

Figure 1



Schematic of the pyrolysis process (in this configuration the required processing energy is obtained by combustion of char), centralized and decentralized logistic schemes, and proposed oil applications.

Table 1

Composition and properties of pyrolysis oils and hydrodeoxygenated (HDO) pyrolysis oils.

Feed Process	1: Pine	2: Pine Pyrolysis		3: Demineralized Pine	4: Pine oil ^d HDO ^a	5: Pine Catalytic pyrolysis
Condensers	Single condenser	Two condensers		Single condenser	–	Single condenser
Conditions	Pyrolysis at: 500°C cond. at 20°C	Pyrolysis at: 500°C 1st cond. at 80°C	Pyrolysis at: 500°C 2nd cond. at 20°C	Pyrolysis at: 500°C cond. at 20°C	HDO at: 400°C 190 bar H ₂ Cat: Ru/C	Pyrolysis at: 450°C Cat: Na-ASA Cond. at 20°C
Oil yield [kg/kg pine] × 100%	63	33	31	66	25	29.7
C [wt%, wet]	40	58	26	38	80	64.6
H	8	7	10	6	10	5.3
O	52	35	64	56	10	29.5
H ₂ O [wt%, wet]	28	2	55	21	1	23.3
Viscosity cp (20°C)	40	>10 000 ^c	3	56	19	–
TAN [mg KOH/g oil]	62	16	81	55	–	–
pH	2.4	2.9	2.2	2.5	–	–
HAc [wt% in oil]	6	1	10	4	–	–
Guaiacol	4	2	2	2	–	–
Levogluconan	5	10	0	24	–	–
Pyrolytic lignin	18	32	0	13	–	–

Data from the University of Twente laboratories [5^{*},6^{*},48,50,52].

^a Hydrodeoxygenation.

^b Column A gives results from condenser 1, Column B for condenser 2.

^c 300 at 80°C.

^d Pine oil of column 1 was the feed.

4. Catalytic upgrading of the oil by, for example hydrodeoxygenation. This lowers the oxygen content and increases the stability for co-refining (see Table 1; column 4 for a typical upgraded oil produced by

hydrodeoxygenation). Recently, many studies are published on co-feeding/co-refining (upgraded) bio-fuels in crude oil refineries [6^{*},7,8] in selected units such as FCC (fluid catalytic cracking), HDS (hydrodesulfurization)

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