



Process development status of fast pyrolysis technologies for the manufacture of renewable transport fuels from biomass



Greg Perkins^{a,b,*}, Thallada Bhaskar^c, Muxina Konarova^d

^a Ventura Energy, Brisbane 4001, Australia

^b Centre for Sustainable Materials and Research Technology (SMaRT), School of Materials Science and Engineering, University of New South Wales, Sydney 2052, Australia

^c CSIR-Indian Institute of Petroleum (IIP), Dehradun 248005, Uttarakhand, India

^d Australian Institute of Bioengineering and Nanotechnology (AIBN), The University of Queensland, Brisbane 4072, Australia

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ABSTRACT

Fast pyrolysis is a promising thermochemical method of producing renewable fuels and chemicals from biomass and waste feedstocks. There is much interest in optimising the choice of feedstock pre-treatments, reaction conditions, reactor designs, and catalysts as well as product upgrading steps to improve the techno-economic feasibility of the process. This article summarizes the current state-of-art in thermal and catalytic fast pyrolysis and outlines the major considerations for process development. The status of process technologies and development efforts on thermal and catalytic fast pyrolysis are reviewed, with a focus on efforts producing bio-oil for use in manufacturing transport fuels or fuel blends as the final product.

The leading thermal pyrolysis processes, which use circulating, bubbling, auger screw and rotating cone reactor technologies, are reviewed alongside recent research and development activities on catalytic fast pyrolysis. This review finds that several technologies for thermal fast pyrolysis are operating at commercial scale, while integrated process development efforts are just starting to focus on applying catalytic fast pyrolysis at pilot scale. Processes for catalytic fast pyrolysis, either via *in-situ* or *ex-situ* upgrading of the bio-oil vapours is an area currently receiving significant research and development interest. This processing route may enable the production of partially upgraded bio-crudes which are suitable for processing to final fuel products in centralized bio-refineries or for co-processing in petroleum refineries. However, there remains a lot of fundamental and laboratory work to be done to develop deeper understanding of the processes, so that the catalysts and reaction conditions can be optimized.

New combinations of unit operations and possibly novel reactors will likely be required to economically convert biomass feedstocks into partially upgraded bio-crudes. Techno-economic assessment shows that bio-fuels from fast pyrolysis may be competitive with petroleum fuels in future, however there are currently only a handful of plants operating commercially.

1. Introduction

Production of fuels from renewable feedstocks and wastes is a potential solution to reducing the environmental impacts of fossil fuel use [1,2], while manufacturing fuels which can be used by the existing infrastructure, including refineries, distribution networks and the existing fleet of vehicles, planes, and ships. The conversion of non-food lignocellulosic biomass feedstocks such as straw, sugarcane bagasse,

wood residues, etc., to fuels and chemicals using thermochemical processes such as pyrolysis, may be a viable [3]. A study by Aston University, UK concluded that “... it should be possible to produce bio-oil for a similar price to mineral oils” [4]. Large scale development of biofuel production from cellulosic biomass to produce liquid fuels could play a role in the transition from today's fossil fuel-based transportation system to a renewable energy system powered largely by electricity in the future [3,5]. It is desirable to produce upgraded bio-oil that is high

Abbreviations: BTG, Biomass Technology Group; BTL, Biomass to Liquid; BTX, Benzene, Toluene, Xylene; CFP, Catalytic Fast Pyrolysis; CPD, Chemical percolation devolatilization; EFB, Empty Fruit Bunch; FP, Fast Pyrolysis; GTI, Gas Technology Institute; HDO, Hydrodeoxygenation; LHV, Lower Heating Value; ICTAC, International Confederation of Thermal Analysis and Calorimetry; IH2, Integrated Hydrolysis and Hydroconversion; MFSP, Minimum Fuel Selling Price; PDU, Process Development Unit; RCFP, Reactive Catalytic Fast Pyrolysis; RCR, Rotating Cone Reactor; RTI, Research Triangle Institute; RTP, Rapid Thermal Processing; TCI, Total Capital Invested; TRL, Technology Readiness Level

* Correspondence to: Ventura Energy, GPO Box 1215, Brisbane 4001, Queensland, Australia.

E-mail address: greg.perkins@venturaenergy.com.au (G. Perkins).

in transportation fuel components such as aromatics and olefins, or which can be blended with existing refinery streams [6]. Biofuel production for aviation, marine, and heavy vehicles has been identified as a medium term opportunity as other renewable alternatives are unlikely to be available anytime soon.

The major challenges in converting lignocellulosic biomass to "drop-in" liquid fuels are related to the feedstock properties. Biomass has a high oxygen content, high water content, and a fibrous molecular structure; also many feedstocks contain a relatively high percentage of alkali salts. As such biomass feedstocks, while containing carbon, hydrogen, and oxygen, are very different from conventional fossil fuels. Feedstock properties, such as low energy density and solid form also make storage and transport more difficult and costly than for conventional hydrocarbon liquid fuels.

The production of renewable fuels from cellulosic biomass and waste sources in biorefineries has involved the study of biological, biochemical and thermochemical routes [7–9]. Recent reviews of the biological routes include anaerobic digestion [10], saccharification and fermentation [11], while biochemical routes include biodiesel production [12,13]. Recent reviews of the thermochemical routes include catalytic cracking [14–17], thermal pyrolysis [3,18–21], catalytic pyrolysis [5,6,22,23], hydro-pyrolysis [24,25], gasification [26–28] and hydrothermal liquefaction [29–34]. The hydrotreating and upgrading of bio-oils to transportation fuel specifications is also of critical interest [18,35–37].

Fast pyrolysis (FP) is a potentially promising thermochemical method of producing renewable fuels and chemicals from biomass and waste feedstocks [20,38–41]. Although it is relatively simple, the main disadvantage is that the resultant bio-oil has many complex properties inherited from the characteristics of the original feedstock, which make it a generally low-grade fuel alternative. Recent reviews show that there is much interest in optimising the fast pyrolysis process by choosing suitable feedstock pre-treatments, reaction conditions, reactor designs, and catalysts as well as product upgrading to improve the techno-economic feasibility of applying pyrolysis processes at large scales to produce commercial quantities of renewable fuels and chemicals [19,21,22,42–46]. An attractive feature of FP is that the biomass can be processed close to the biomass source to produce a densified fuel (ie. bio-oil) which can be transported to existing refineries or new bio-refineries for upgrading into finished fuels and chemicals. Heterogeneous catalysis can be applied during fast pyrolysis to upgrade the bio-oil quality and/or to improve the selectively to valuable fuel and chemical components [47].

The objective of this article is to summarize the current status of process technologies and development efforts related to fast pyrolysis of biomass, with a focus on the commercial production of bio-oil for use in manufacturing transport fuels as the final product. This review will look at the challenges from a perspective of process development. As such, the article will start with a summary of thermal fast pyrolysis, an outline of the considerations for process development and then make a review of existing technologies and contemporary development efforts on thermal and catalytic fast pyrolysis (CFP) focusing on efforts already at pilot and demonstration scale. The article will conclude with an overview of the technology readiness levels for the leading processes and a summary of recent techno-economic assessments.

2. Fast pyrolysis

2.1. Overview

Biomass is a mixture of hemicellulose, cellulose, lignin, and various other minor amounts of organics which degrade and pyrolyze at different rates and by different mechanisms and pathways [48,49]. Pyrolysis involves thermal decomposition of carbonaceous material when heated in the absence of oxygen to form a range of products including light gases, char, water, and oil. Pyrolysis is usually characterised based

Table 1
Modes of pyrolysis (learned from Bulushev et al. [45]).

Mode	Temperature (°C)	Residence Time (seconds)	Yields (wt%)		
			Liquid	Gas	Char
Slow	450	Very long (> 30 s)	30 (70% water)	35	35
Medium	500	Moderate (10–30 s)	50 (50% water)	25	25
Fast	500	Short (< 2 s)	70 (30% water)	12	13
Flash	500	Very Short (< 0.5 s)	75 (25% water)	< 12	< 13
Gasification	> 800	Long	5	85	10

on the residence time of the biomass and the operating temperature as seen in Table 1. Slow pyrolysis involves very long residence time of the biomass and yields mostly gas and char. Medium pyrolysis is typically undertaken with residence times of the order of tens of seconds and results in improved liquid yields. Fast pyrolysis refers to residence times which are less than a few seconds and this gives maximum liquid yields of up to 75 wt%, with relatively low amounts of gas and char [50].

Pyrolysis is performed in the temperature range of 400–600 °C and when the temperature is increased above 750 °C, then gasification reactions become significant and most of the biomass gets converted to gases (predominately CO, CO₂, H₂, and CH₄) [50]. According to Mohan et al. [51], the general changes that occur during pyrolysis of a biomass particle are:-

1. Heat transfer from external heat source to the fuel to proceed the pyrolysis reaction
2. High temperature pyrolysis of primary vapours leads to volatiles and forms char
3. Heat transfer between unpyrolyzed fuel and hot volatiles due to the flow of pyrolysis hot vapours towards solid biomass particles.
4. Tar can be produced due to the condensation of the volatiles and the consequent secondary reactions, in parts of biomass solid particles that are still cooler
5. Together with primary pyrolytic reactions (item 2) autocatalytic secondary pyrolysis reactions occurs in competition; and
6. Depending upon process parameters such as residence time, pressure and temperature; other reactions including decomposition, water gas shift, radicals recombination, reforming and dehydrations can take place.

Fig. 1 shows a schematic of the main reaction pathways during wood pyrolysis. Recent research has shown that an intermediate liquid forms during pyrolysis [52]. The yields of liquids are maximized with high solid heating rates, short vapour residence times, and temperature of circa 500 °C [53]. These conditions aim to prevent: i) the primary

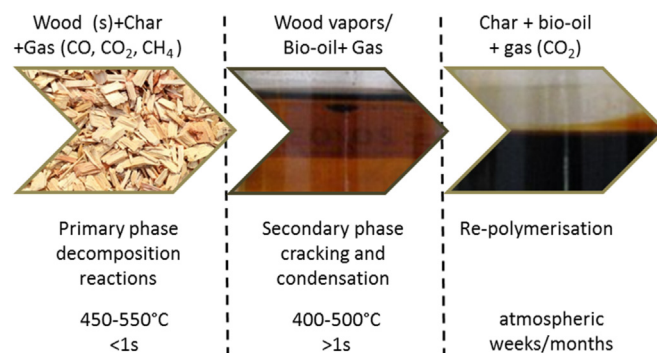


Fig. 1. Summary of reaction pathways for wood pyrolysis.

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