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Recent advances on fast hydrolysis of biomass

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ABSTRACT

Even though hydrolysis of biomass has been studied for many years, it was characterized by long residence times and low heating rates. On the other hand, fast hydrolysis, the rapid decomposition of an organic material under a hydrogen atmosphere, has been primarily reported only over the last five years. There is growing interest in the topic, and this brief article reviews fast hydrolysis of biomass, describing previous findings, current challenges, and research opportunities for the future. The current literature shows that catalytic fast hydrolysis produces primarily aromatic hydrocarbons, but alkanes and naphthenes can also be produced under appropriate conditions if a secondary unit is added for hydrotreating (ex-situ upgrading). Compared to catalytic fast pyrolysis, the higher yields of hydrocarbons and much slower catalyst deactivation due to coking promising. Yields in the range of 80–95 gal/t can be obtained, and the process economics is equivalent to those of other biofuel processes, such as fast pyrolysis followed by hydrotreating/hydrocracking.

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1. Introduction

Liquid fuels for transportation constitute a large fraction of the fuels used worldwide. The world consumption of liquid fuels in 2010 was roughly 87 million barrels/day [1]. With a few exceptions, these liquid fuels are mixtures of hydrocarbons, which are convenient for use and have a high hydrogen content and volumetric energy [2,3]. Transportation fuels are currently obtained from fossil resources, but there is great interest in producing a portion of those fuels from renewable resources. Biomass is one of the few possible sources of renewable carbon, and therefore the most likely source of renewable liquid fuels [4] (CO₂ is another potential source). The Energy Independence and Security Act (EISA) of 2007 requires the US to produce 36 billion gallons of renewable fuels/year by the year 2022 [5,6]. This number corresponds to about 25% of the annual consumption of gasoline in the US [7].

Several processes have been proposed to produce liquid fuels from lignocellulosic biomass, and fast pyrolysis is one of the most promising ones. Fast pyrolysis is the rapid thermal degradation of organic materials in the absence of oxygen, at rates in the range of 500 °C/s, to a final temperature of 500–600 °C [8]. The rapid heating decomposes the large molecules of biomass into smaller ones, which are released in the form of volatile compounds. The volatiles are then quickly cooled back to room temperature, generating a brownish liquid fuel, usually referred to as “bio-oil”. Up to 75 wt%

of the original biomass can be collected as bio-oil. About 12 wt% of char, and 13 wt% of permanent gases (CO, CO₂, CH₄) are also produced [9,10]. The key to maximize liquid product yield is a short residence time for the volatiles (usually a few seconds), in order to prevent secondary cracking reactions [9].

Bio-oil can be used for applications such as heating, electricity generation, and chemicals production [10–12]. Its use as a transportation fuel, however, remains problematic because of properties associated to the high level of oxygen in the fuel. The oxygen content in the bio-oil is roughly 35–40 wt%, which leads to a higher heating value (HHV) of about 17 MJ/kg, compared to 42–44 MJ/kg of conventional gasoline and diesel. In addition, bio-oil is not miscible with conventional hydrocarbon fuels, has high acidity (pH 2–3, total acid number TAN 100–200), which makes it corrosive to materials of construction—usually TAN lower than 2 is required for transport vessels and refinery conversion equipment [13]. Bio-oil is also unstable because of reactive components such as acids, aldehydes and ketones, which cause polymerization over time and increase the viscosity (this process is called “aging”) [9,14]. It is believed that temperatures as low as –20 °C are required to stop the chemical mechanisms involved in the aging of the oil [15]. Another problem is the high water content mixed with the oil, usually about 25 wt%, which decreases the heating value and causes ignition delay [14,16]. Due to these characteristics, the demand for fast pyrolysis oil is low [17].

Despite the unfavorable properties, bio-oil can be upgraded to liquid hydrocarbons that are compatible with the infrastructure used for transportation fuels, and this is performed by removal of

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Table 1
Summary of previous works on fast hydrolysis of biomass.

References	System	Feedstock	Reactor temp. (°C)	Hydrotreating temp. (°C)	Pressure (bar)	Catalyst
[44,51]	Py-GC/MS with hydrotreating	<i>Miscanthus × giganteus</i>	600	300–450	Atmosph.–30 bar	ZSM-5, Ni/ZSM-5, MCM-41, Ni/MCM-41 (hydrot.)
[20,26]	Py-GC/MS	Pine wood	650	–	5.5–28.0	HZSM-5, Co/ZSM-5, Ni-ZSM-5, Pt-ZSM-5 (hydrop.)
[50]	Py-GC/MS	Lignin	650	–	Atmosph.–25.8	Pd/HZSM-5 (hydrop.)
[49]	Fluidized Bed	Woody residue	375–450	–	3.4–20.0	Proprietary (hydrop.)
[52,53,61]	Fluidized Bed with single shot for feed	Rice husk	450–650	–	Atmosph.	Ni/LY, Ni/Al ₂ O ₃ , dolomite, CoMo/Al ₂ O ₃ (hydrop.)
[17,45]	Fluidized Bed with hydrotreating	Several	343–469	343–399	19.5–22.4	Proprietary (hydrop.)
[1,46]	Cyclone with hydrotreating	Cellulose, poplar	480–580	300–375	27–54	Al ₂ O ₃ , 2% Ru/Al ₂ O ₃ , 2% Pt/Al ₂ O ₃ , 5 wt% Pt–2.5 wt% Mo/MWCNT (hydrot.)

oxygen atoms. The most commonly studied option in the past was hydrotreating, which consists of re-evaporating the oil and reacting it with H₂ at very high pressures (100–170 bar), 310–375 °C [18], and low space velocities (0.1–0.2 LHSV), and it typically requires a sulfide CoMo or NiMo catalyst supported on alumina [19,20]. Hydrotreating usually requires adding about 3–5 wt% of H₂ relative to the mass of bio-oil, obtaining a hydrogenated liquid corresponding to 26–30 wt% of the original biomass [13], or 58 wt% of the liquid bio-oil [21]. However, this process would be expensive and slow. Single stage hydrotreatment is considered an inappropriate method for upgrade, because of the formation of large quantities of coke, leading to rapid catalyst deactivation and reactor clogging [18].

In recent years, significant attention has been devoted to catalytic fast pyrolysis as a method for producing hydrocarbons from biomass. In this case, fast pyrolysis is performed in the presence of a catalyst, usually a zeolite [22–25]. The pyrolysis volatiles are upgrade in-situ via dehydration, decarboxylation, and decarbonylation reactions. Since a significant amount of the oxygen is released in the form of water, a large amount of hydrogen atoms are removed from the liquid product, leading to aromatic hydrocarbons and some light olefins. The great advantage of catalytic fast pyrolysis is that H₂ is not required, and a stable liquid product is formed [26]. However, at best only 20–30% of the carbon in the biomass ends up in the liquid product. Roughly 30% of the carbon goes to coke, causing catalyst deactivation [27].

In this review, we discuss hydrolysis of biomass, which is the decomposition in the presence of H₂ [3]. Hydrolysis has been studied initially for coal [28–33], and later to generate hydrocarbons from biomass [34–43]. In hydrolysis, the reducing H₂ gas generates hydrogen radicals which react with volatiles released by the biomass, usually in the presence of a catalyst, removing oxygen which can be released in the form of water, CO, and CO₂, and producing hydrocarbons. Additionally, many of the reactive volatile intermediates are capped by the hydrogen radicals. These intermediates would otherwise undergo polymerization, so the addition of H₂ lowers the possibility of coking on the catalyst [20,44]. One of the advantages of hydrolysis is that the pressures required are typically much lower than what is needed to hydrotreat bio-oil (about 30 bar compared to 100–170 bar for bio-oil hydrotreating) [17,45]. Another interesting characteristic of hydrolysis is that the process is exothermic, generating heat which helps sustain endothermic pyrolysis reactions that take place in the reactor [17].

Prior to 2010, most of the work reported for hydrolysis of biomass focused on batch and fixed bed reactors operating at low heating rates and long residence times [34–42] (here, we refer to this as slow hydrolysis). These conditions, however, are not consistent with the need for low residence times with rapid heating and cooling which are typical of fast pyrolysis systems [46], and the oxygen content of the oil obtained is still about 20 wt%

[41]. Fast hydrolysis, on the other hand, is analogous to fast pyrolysis, with the main difference being the presence of a H₂ atmosphere. Two recent reviews on hydrolysis have been published [4,47] and describe extensively the previous work with slow hydrolysis. Another review from GTI researchers [48] focuses on the integrated hydrolysis plus hydroconversion (IH²) process they developed. Recent research efforts have been focused on hydrolysis systems that resemble fast pyrolysis systems in terms of heat transfer rates and vapors residence time, referred as fast hydrolysis. The present review discusses the recent findings and developments on this process.

2. Process description

Fast hydrolysis is the decomposition of an organic material under high heating rates (about 500 °C/s) in a H₂ environment [1]. It can only be performed in systems that allow short vapor residence times (a few seconds), such as fluidized bed reactors [17,45,49], cyclone reactors [1,46], and microhydrolysis systems such as Py-GC/MS (pyroprobe) [20,50]. The H₂ may be the only gas, or may be diluted in an inert gas such as N₂. Fast hydrolysis was performed for coal in the past [28–30], and to the best of our knowledge, it was reported first for biomass by Steinberg and Division [34] in 1986. However, the temperatures employed in that work were very high (600–1000 °C), so that CH₄ and CO were the major products. In this review, we are concerned with fast hydrolysis in the range 350–650 °C, which focuses on maximizing yields of liquid hydrocarbons. The H₂ partial pressure is variable, and it usually ranges from atmospheric to about 30 bar, though studies with 54 bar have been reported [46]. The process can be catalytic or non-catalytic—however, in order to ensure proper level of deoxygenation, some groups have employed a hydrotreating unit right after the fast hydrolysis reactor, so that the volatiles coming from the first reactor are immediately upgraded in the second unit [1,17,45,46]. This is referred to as ex-situ hydrotreating. Table 1 shows a summary of the works in the literature on fast hydrolysis of biomass.

Fast hydrolysis generates two liquid phases: an organic phase containing a mixture of hydrocarbons which is the target product, and an aqueous phase, along with char and permanent gases. If a catalyst is used, then coke on the catalyst surface may also be produced, though it has been reported that coke formation is small [17]. Fig. 1 shows the possible configurations for the catalyst, the fast hydrolysis reactor, and the hydrotreating reactor. A fluidized bed reactor is chosen for the purpose of this illustration. All the configurations are discussed next: non-catalytic fast hydrolysis, catalytic fast hydrolysis, non-catalytic fast hydrolysis with ex-situ hydrotreating, and catalytic fast hydrolysis with ex-situ hydrotreating.

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