



## Full Length Article

## Two-stage catalytic fast hydrolysis of biomass for the production of drop-in biofuel

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## ABSTRACT

The major obstacles for the production of drop-in fuel from traditional fast pyrolysis are low bio-oil yield, poor fuel heating value and high solid yield. To overcome these obstacles, we studied the introduction of high pressure hydrogen into the pyrolysis reactor, in a process known as catalytic fast hydrolysis (CFHP). CFHP of anisole, a bio-oil model compound, was performed at different temperatures and pressures, to determine the effects of those variables on the CFHP reaction network. Alkanes were observed at low temperature and high pressure, whereas aromatics were dominant at low pressure and high temperature. Aspen modelling and calculation of reaction equilibrium constants showed that there is a thermodynamic barrier for simultaneous pyrolysis and hydrogenation at 600 °C. Reduced heating rates and CFHP followed by second-stage hydro-processing (SH) were proposed as a means to control reaction temperature and efficiently deoxygenate CFHP vapors. The two-stage CFHP followed by hydroprocessing produced nearly 18 mol% carbon yield to alkanes, and a total bio-oil carbon yield of 25 mol%. The approximate bio-oil higher heating value (HHV) and aromaticity were 43.4 MJ/kg and 28 wt%, respectively, both within the range of gasoline.

## 1. Introduction

There are several pathways for the conversion of lignocellulosic biomass to fuels. Among them, thermochemical conversion is perhaps the most readily accessible and closest to commercialization [1,2]. Liquid fuel produced from biomass is sustainable, renewable, and near carbon-neutral [3,4]. Moreover, given the recent emphasis on U.S. energy independence, biomass is a plentiful, local raw material, which can supplement crude oil for hydrocarbon fuel production.

Biomass fast pyrolysis is the thermal decomposition of biomass at high heating rates and intermediate temperature (typically 400–600 °C), under inert atmosphere [5]. At these conditions, the polymeric cellulose, hemicellulose and lignin fractions of the biomass fragment to form volatile bio-oil products, in addition to char and permanent gas [6]. The bio-oil produced from fast pyrolysis is an unstable mixture of low-energy oxygenated hydrocarbons, which must be upgraded prior to use as a transportation fuel [7]. Catalyst upgrading may occur either *ex-situ* or *in-situ* the pyrolysis reactor, in a process known as catalytic fast pyrolysis (CFP) [8]. Of the many possible upgrading catalysts, ZSM-5 zeolite has been identified as the preeminent choice due to its proper pore structure, excellent hydrothermal stability and tunable acidity [9]. Hydrocarbon yields between 15 and 25 wt% of the initial biomass are typically reported from ZSM-5 catalyzed CFP

[10]. Many research groups have focused on ZSM-5 catalyst modifications for CFP [11–14], and have demonstrated the feasibility of producing bio-oil with greatly reduced oxygen content [15].

However, low bio-oil yields, carbon loss to solids and permanent gas, as well as low bio-oil heating value are major obstacles, which must be minimized in order to make the fast pyrolysis process viable. Moreover, a substantial majority of hydrocarbons formed from CFP are aromatic in nature, while traditional gasoline typically contains about 25 wt% aromatics [16]. Use of benzene was specifically limited in 2011 by the U.S. Environmental Protection Agency due to environmental health and safety concerns [17].

To illustrate the stages of the pyrolysis and upgrading process, Fig. 1 presents a Van Krevelen diagram of the relative oxygen, hydrogen and carbon contents of each component during the thermochemical transformation of biomass to fuels. Raw biomass is rich in oxygen, some of which is removed as water, CO and CO<sub>2</sub> after pyrolysis alone [5]. The bio-oil may then be upgraded over an acid catalyst to form a more stable blend of aromatic hydrocarbons and low levels of oxygenates [14]. However, due to the hydrogen depleted environment during pyrolysis, even the most deoxygenated bio-oil has an atomic H:C ratio of about 1, which more closely resembles the H:C ratio of coal, rather than a typical petroleum blend. Hydrodeoxygenation (HDO) must be performed on the upgraded bio-oil to improve higher heating value

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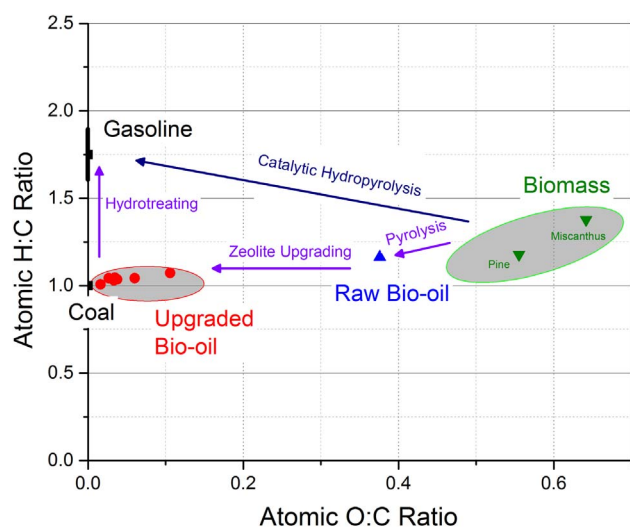


Fig. 1. Van Krevelen diagram illustrating the relative hydrogen, carbon and oxygen contents of each step of the transformation of biomass to fuels via catalytic pyrolysis. All bio-oil atomic calculations are on a dry-basis. Raw bio-oil calculation from Bridgwater et al. [5], Upgraded bio-oil calculated from bio-oil produced by Gamliel et al. [14], gasoline product calculation from Morvay and Gvozdenac [18].

(HHV), remove remaining oxygen heteroatoms and bring the total H:C ratio closer to 1.75 [18]. Supported NiMo and CoMo [19,20], transition and precious metals [21,22], and supported bi-metallics [23] have been shown to be effective hydrogenation/deoxygenation catalysts. Nevertheless, substantial work is still necessary to maximize HDO catalyst effectiveness, reduce process energy intensity and limit overall hydrogen consumption [24]. In this work, we explore the feasibility of catalytic fast hydrolysis (CFHP) as a means to circumvent this cycle, and produce high returns of renewable alkanes and aromatics from lignocellulosic biomass in a single- or two- step catalytic process.

CFHP is the catalytic pyrolysis of biomass at high heating rate under a pressurized hydrogen atmosphere [25]. The presence of hydrogen in the CFHP reactor increases carbon efficiency by shifting reaction pathway from decarbonylation and decarboxylation to dehydration, thus removing oxygen in the form of water [26]. Inclusion of a ZSM-5 catalyst in the CFHP reactor assists in pyrolysis vapor deoxygenation and char reduction [8,9,27], while the presence of a transition metal, such as Ni or Ru may assist in hydrogenation and HDO reactions [28].

One of the primary tools for studying CFHP catalysis and operating conditions is pyrolysis gas chromatography (PyGC) [29–32]. The PyGC technique is commonly applied for rapid screening of catalysts and process conditions, such as the effects of pyrolysis atmosphere, temperature, and pressure [33]. Thangalazhy-Gopakumar et al. [31,34] have performed CFHP of pine at 650 °C and 28 bar in a PyGC unit over various metal-ZSM-5 catalysts. They showed that ZSM-5 is effective for deoxygenation, but no hydrogenated products were observed from CFHP with any of the metal-impregnated catalysts tested. Melligan et al. [29,30] performed hydrolysis of miscanthus at 600 °C, followed by second-stage upgrading in a low temperature fixed-bed reactor over Ni-ZSM-5 catalyst. They found that alkane yields and selectivity increase at higher hydrogen pressure. Jan et al. [32] studied both single-stage lignin CFHP and hydrolysis followed by second-stage hydrotreating using Pd-ZSM-5 catalyst. It was concluded that alkane formation is thermodynamically unfavorable during single-stage CFHP, and *ex-situ* upgrading was necessary.

The goal of this work is to understand the factors that drive CFHP product selectivity towards true ‘drop-in’ fuel compounds, consisting of a blend of aliphatic and aromatic hydrocarbons. The effects of reaction pressure and temperature are systematically explored by performing CFHP of anisole, a common bio-oil model compound [35], at a range of operating conditions. The thermodynamic barrier for hydrogenation in

the context of CFHP vapor upgrading is discussed. Finally, two process modifications to overcome these barriers are proposed and tested: (1) reduction of CFHP heating rate and (2) CFHP followed by second-stage hydroprocessing (SH).

## 2. Materials and methods

### 2.1. Material preparation

ZSM-5 zeolite, with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 80 was purchased from Zeolyst International (CBV 8014). Silica support was purchased from Sigma-Aldrich. All materials were calcined at 550 °C for 6 h prior to use. Ni was incorporated on both SiO<sub>2</sub> and ZSM-5 via incipient wetness impregnation [36], using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich). Bulk Ni loading was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) to be 4.42 wt% on the ZSM-5 (4%-Ni-ZSM-5) and 4.05 wt% SiO<sub>2</sub> (4%-Ni-SiO<sub>2</sub>) support. All Ni-impregnated materials were calcined and then reduced at 450 °C in pure hydrogen for 4 h prior to use. Further information about catalyst characterization, including acidity and textural properties, can be found in a previous work [37].

### 2.2. Catalytic hydrolysis of anisole and miscanthus

All CFHP experiments were performed in a PyGC unit (CDS Analytical 5200HP). Scheme 1 shows a schematic of the PyGC system. Pyrolysis and upgrading reactions occurred in a quartz tube micro-reactor (1.9 mm I.D., 25 mm length), and/or a downstream fixed-bed reactor (3.5 mm I.D., 85 mm usable length). Ar (UHP 300, Airgas) was used as the purge gas for all experiments. Pressure was maintained by a back-pressure regulator downstream of the pyrolysis interface, which was adjusted to the desired operating pressure +/- 0.2 bar prior to the experiment. Carrier gas flow rate was monitored by a flowmeter placed at the outlet of the unit. The microreactor heating rate set-point was 999 °C/s, unless specified otherwise. All lines were maintained at 300 °C to prevent condensation of pyrolysis vapors. Condensable products were captured on a cold adsorption column (Tenax, Dow Chemical), and permanent gas travelled through the unit outlet to an online mass spectrometer (MS).

In order to study the effects of CFHP operating temperature and pressure, anisole (99% purity, Sigma-Aldrich) was employed as a bio-oil model compound. Anisole is an ideal choice for model compound due to the moderate volatility and the presence of a methoxy group (–OCH<sub>3</sub>), common in lignin-derived phenols [38–40]. Anisole is a frequently studied bio-oil model compound [41]. For these experiments, 10 mg of 4%-Ni-ZSM-5 catalyst was loaded into the downstream fixed-bed reactor, held in place by two slugs of quartz wool. Catalyst was reduced *in-situ* for 30 mins at 450 °C in pure hydrogen (Airgas, UHP300). The system was then purged with Ar, and the reactor was brought to the operating temperature and pressure dictated by the experiment. Exactly 0.8 μL of anisole was injected into a bead of quartz wool placed inside the quartz microreactor, using a GC syringe. The loaded microreactor was placed in the resistively-heated coil probe, and then quickly inserted into the pyrolysis interface. The system was purged with hydrogen for 5 mins, followed by heating of the interface and probe to 300 °C to vaporize the anisole (boiling point of 154 °C). Anisole was transported by the hydrogen to the fixed-bed reactor (flow rate of 110 ± 5 sccm), and the reactor effluent was swept to the cold trap. The gas hourly space velocity (GHSV) was approximately 520,000 h<sup>-1</sup>. Gas and liquid products were analyzed using the methods outlined below. For simplicity, the total conversion for anisole CFHP was defined as the sum of the mass yields of GC detectable liquid compounds, CO, CO<sub>2</sub> and CH<sub>4</sub>. Spent catalyst was tested for coke deposition using temperature programmed oxidation (TPO) in a Netzsch STA 449 F3 Jupiter thermal analyzer, but no discernable levels of coke were formed on the catalyst, and as such solid yield was not quantified.

In this study, *Miscanthus x giganteus* was chosen as the biomass of

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