



## Full Length Article

# Biomass pyrolysis gas conditioning over an iron-based catalyst for mild deoxygenation and hydrogen production



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## ABSTRACT

Bio-crude is a renewable source for production of valuable energy carriers. Prior to its utilization, a conditioning step of the raw pyrolysis gas can be beneficial before the bio-crude is converted via catalytic hydrodeoxygenation (HDO) into liquid hydrocarbon products, or via steam reforming (SR) to synthesis gas/hydrogen. An experimental small industrial-scale study for the chemistry of atmospheric pressure pyrolysis gas conditioning resulting in bio-crude deoxygenation and a hydrogen-rich gas is presented and discussed. This study is performed using an iron-based catalyst without addition of hydrogen or steam. Following a short catalyst stabilization period with fluctuating bed temperatures, the catalyst operated near 450 °C at a space velocity of 1100 h<sup>-1</sup> for 8 h under stable conditions during which no significant catalyst deactivation was observed. Experimental results indicate a 70–80% reduction of acetic acid, methoxy phenols, and catechol, and a 55–65% reduction in non-aromatic ketones, BTX, and heterocycles. Alkyl phenols and phenols were least affected, showing a 30–35% reduction. Conditioning of the pyrolysis gas resulted in a 56% and an 18 wt% increase in water and permanent (dry) gas yield, respectively, and a 29% loss of condensable carbon. A significant reduction of CO amount (–38%), and production of H<sub>2</sub> (+1063%) and CO<sub>2</sub> (+36%) over the catalyst was achieved, while there was no or minimal change in light hydrocarbon content. Probing the catalyst after the test, the bulk phase of the catalyst was found to be magnetite (Fe<sub>3</sub>O<sub>4</sub>) and the catalyst exhibited significant water gas shift (WGS) reaction activity. The measured gas composition during the test was indicative of no or very limited Fischer-Tropsch (FT) CO/CO<sub>2</sub> hydrogenation activity, and this infers that the active surface phase of the catalyst during the test also was Fe-oxide, rather than Fe-carbide. The results show that iron-based materials are potential candidates for application in a pyrolysis gas pre-conditioning step before further treatment or use, and a way of generating a hydrogen-enriched gas without the need for bio-crude condensation.

## 1. Introduction

In recent decades, it has become evident that fossil fuels resources are depleting and that CO<sub>2</sub> emissions are partly responsible for global warming [1]. At the same time, the demands for energy supply has never been higher worldwide due to an increasing population and way of living [2,3]. The use of biomass to produce valuable energy carriers is one possible pathway for reducing the impact of present energy usage, as well as the dependency on fossil fuels [4]. Biomass can be converted into liquid, gas, and char via pyrolysis [5–9]; these products may then be utilized for different purposes. The pyrolysis bio-crude, *i.e.*, the liquid condensate predominantly consisting of oxygenated organic compounds (oxygenates), is problematic to handle and exploit, and removal/conversion of oxygenates is needed.

While catalytic pyrolysis and hydrodeoxygenation (HDO) aim to

deliver an oil refinery compatible feedstock and a completely deoxygenated liquid, respectively, severe coking and deactivation of the catalysts employed generally limit their industrial implementation [10]. Therefore, a conditioning step of the raw pyrolysis product before further processing can have many benefits from a process point-of-view.

The full gas phase composition from the pyrolyzer is in this work referred to as pyrolysis gas, *i.e.*, the permanent gases together with the bio-crude oxygenates and water in the gaseous state. Mild (or partial) oxygenate deoxygenation lowers the pyrolysis gas dew point temperature, thus lowering the risk of unwanted condensation in process equipment, and also reduces the corrosive and polymerizing power of the condensate [11,12]. Furthermore, catalyst deactivation by carbon laydown in catalytic steam reforming due to particularly troublesome classes of oxygenate compounds, such as heterocycles, methoxy phenols, and phenols [13], may be circumvented. After such a conditioning

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step, the bio-crude may be treated with hydrogen at high pressure and converted to suitable hydrocarbon products via catalytic HDO [8,14–17] or catalytically cracked and steam reformed in SR, optionally followed by a separate lower temperature water-gas shift (WGS) step, into a synthesis gas [18–23].

Furthermore, concepts for bio-crude conditioning during hydro-treatment are previously reported [24]; however, all concepts reported utilize condensed bio-crude, as well as high hydrogen pressures, increasing the overall processing costs. An online conditioning step would be superior as re-evaporation of thermally labile bio-crude is not required. Moreover, atmospheric pressure treatment without the addition of external hydrogen at high pressure or steam minimizes additional costs.

In the present study, the concept of online mild catalytic treatment of pyrolysis gas over an iron-based catalyst without the addition of external hydrogen or steam is considered. Previous laboratory-scale studies on catalytic flash pyrolysis [14,16], catalytic upgrading of pyrolysis vapors [25–27], as well as model compound studies [28,29], indicate that Fe-based catalysts are interesting as low-cost materials for oxygenate deoxygenation/conversion at intermediate temperatures. We investigated the potential of using a Fe-based catalyst for conversion of pyrolysis gas (bio-crude and permanent gas), produced in an industrial small-scale pyrolyzer, for production of less oxygenated liquid and hydrogen-enriched gas as a pre-conditioning step before further treatment. To the best of the authors' knowledge, no such concept has been investigated previously at industrial scale. Other materials such as zeolites have been extensively used for bio-crude deoxygenation and upgrading, achieving high degrees of deoxygenation [30]. However, major components of bio-crude (i.e., phenols) have low reactivity on ZSM-5 (a zeolite catalyst) and undergo thermal decomposition producing coke. Zeolite catalysts also deactivate quickly by carbon laydown from the decomposition and polymerization of large organic molecules present in the bio-crude [14,31]. Therefore, zeolites need frequent regeneration and their use in a fixed-bed reactor is therefore problematic. In addition to the coking problem, most employed zeolite materials are water sensitive at elevated temperatures and the resulting dealumination causes irreversible deactivation [14].

The current study focuses on general process performance and the chemistry taking place on the Fe-based catalyst surface. Specifically, the catalyst activity toward pyrolysis vapor conversion to permanent gases and non-oxygenated hydrocarbons as well as the WGS reaction properties are evaluated by comprehensive analysis of changes in bio-crude and permanent gas composition, as well as by characterization of fresh and spent catalyst. In addition, reaction pathways of the pyrolysis gas catalytic reforming are proposed.

## 2. Experimental

### 2.1. Experimental setup

All experiments were performed at Cortus Energy AB biomass gasification facility in Köping, Sweden [32]. The experimental setup was installed on site and utilized the gas produced from the pyrolysis reactor. The pyrolysis reactor consists of a rotary kiln where dried biomass is fed and pyrolyzed at a temperature of 380 °C and at slow heating rates (approx. 15 °C/min). The resulting char is ground and fed to an indirectly heated steam gasifier, while the pyrolysis gas is transferred to burners in a heated line (pyrolysis gas line) and combusted to produce the heat required for steam gasification. The setup, designed and developed at KTH Royal Institute of Technology, is schematically shown in Fig. 1. It consists of four main parts; a high-temperature filter, a fixed-bed catalytic reactor, piping and valves, and a sampling system. A simple block diagram of the sampling system is shown separately in Fig. 2. All piping and valves were heated and insulated to avoid condensation along the tubes. All piping and valves were trace heated to avoid condensation along the tubes and all the heated parts were

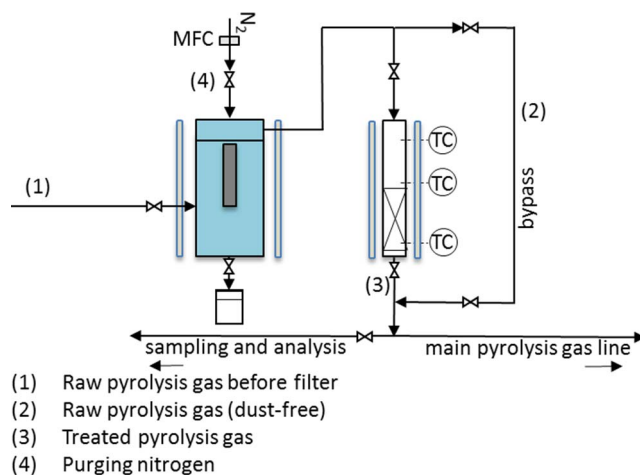


Fig. 1. Schematic of the experimental setup.

insulated to minimize the heat loss. The hot gas filter was used to remove particulates from the raw pyrolysis gas (line 1) before entering the catalytic reactor. The filter was heated externally and purged with nitrogen periodically (line 4) to avoid build-up of a filter cake and a consequential pressure drop. The dust-free pyrolysis gas (line 2) could either bypass or enter the catalytic reactor. The volume of the reactor was 2.3 dm<sup>3</sup> and had an inner diameter of 55 mm. The reactor was externally heated using three heating zones with a height of approximately 0.3 m each, controlled by the reactor wall temperature. Three thermocouples monitored the temperature inside the reactor.

Sampling of the pyrolysis gas was done with a known dry gas sampling flow of 2 l/min. The system enabled both sampling of condensate (bio-crude and water) and permanent gases (N<sub>2</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2+</sub>) mixture before and after the catalytic reactor. C<sub>2+</sub> compounds, measured by GC, were C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and 1-butene. The first two and the last impinger bottles contained iso-propanol, while the rest of the bottles in the sequence contained water. The first three impinger bottles with glass frit were placed in a cooling water bath, enabling rapid condensation of the bio-crude and water, as well as preventing evaporation of the iso-propanol. The application of a low sampling rate helps minimize losses due to evaporation, and flow rates from 1.7 to 10 l/min are recommended [33]. The use of impinger bottles with glass frit is needed for the breakdown of aerosols possibly formed during the cooling of the pyrolysis gas [33]. Moreover, the use of alcohol in the cooled impinger bottles also helps to minimize their formation during the condensation [34]. The last two impinger bottles were added for further cooling of the pyrolysis gas. A phosphorous pentoxide column was placed before the GC to remove any remaining moisture.

### 2.2. Materials and methods

#### 2.2.1. Materials

The tests were carried out using chips of treetops and branches (GROT). The composition of the biomass is listed in Table 1. The catalyst used for experiments was an unsupported Fe-based catalyst (Haldor Topsoe A/S, HT-25409) with a cylindrical pellet shape form of 6 × 6 mm size. Inert filler (Vereinigte Füllkörper-Fabriken, DURANIT® Inert Balls D99 with the size of 1/8") was used in the volume of the reactor above and below the catalytic bed to increase the thermal conductivity, as well as improving radial mixing, reducing the axial dispersion and minimizing channeling over the catalytic bed.

#### 2.2.2. Gas and condensate analysis

The composition of the permanent gases in the pyrolysis gas, i.e., after condensing out water and the bio-crude, was analyzed using an online micro-GC (Thermo Scientific, C2 V-200). The C/H/O and S

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