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Oxidative steam reforming of pyrolysis oil aqueous fraction with zirconia pre-conversion catalyst

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ABSTRACT

Hydrogen was produced via steam reforming and oxidative steam reforming of a pyrolysis oil aqueous fraction, which was obtained via fractional condensation. The steam reforming experiments were carried out using a commercial nickel catalyst with and without a zirconia monolith as a pre-conversion catalyst. Addition of oxygen, which was examined at four different oxygen-to-carbon ratios, resulted in linearly decreasing H₂ yields using both catalyst combinations. The combined effect of the zirconia pre-conversion catalyst and the oxygen addition did, however, slow down the rate at which the H₂ yield decreased during the 4 h experiments. A long term experiment at the previously determined optimal conditions showed that the H₂ yield decreased clearly more rapidly than carbon conversion. The decrease in the H₂ yield was accompanied by a decrease in the selectivity towards CO₂, and consequent increases in the selectivities of CO, CH₄ and C₂ hydrocarbons. These changes indicated that the catalyst was continuously losing its activity towards the reforming of hydrocarbons and conversion of CO via the water-gas shift reaction.

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Introduction

Fast pyrolysis is a technology that can be used for converting solid lignocellulosic biomass into a liquid product commonly referred to as pyrolysis oil or bio-oil. Pyrolysis oil, which is formed via thermal decomposition of the individual biomass constituents, is a complex mixture consisting of thermal degradation products of cellulose, hemicellulose and lignin, and typically up to 30 wt% of water [1–3]. Although crude pyrolysis oil can be used as a boiler fuel [4], its utilization in

more demanding applications necessitates a certain degree of upgrading. These upgrading processes are typically designed to alleviate the challenging properties of pyrolysis oil by converting it into a form which bears more resemblance to the liquid hydrocarbon fuels that are commonly used today. This kind of transformation can be facilitated by using catalytic upgrading technologies. Among the various upgrading routes, catalytic hydrodeoxygenation (HDO) is considered as one of the most comprehensively studied options [5,6]. One of the more challenging aspects of pyrolysis oil HDO is, however, the high hydrogen consumption associated with it [7,8]. Producing

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the necessary hydrogen from a fossil feedstock such as natural gas, can have an adverse effect on the greenhouse gas reduction potential of the entire fuel production route. Therefore, having a renewable source of hydrogen, and limiting the hydrogen consumption of the HDO process while still retaining the desired product quality, are both factors with a positive effect on the hydrogen economy of this concept.

Although whole pyrolysis oil can be upgraded to liquid hydrocarbons via HDO, one should bear in mind that pyrolysis oil is a very heterogeneous mixture on the molecular level. It contains a wide array of oxygenate compounds with various organic functionalities and molecular sizes [9]. The lighter end of the pyrolysis oil product spectrum contains large amounts of water-soluble low molecular weight oxygenates. This group consists mainly of acids, aldehydes and ketones, alcohols, furans and monomeric phenols. Due to the limited carbon chain length that many of these compounds possess, their complete hydrodeoxygenation/hydrogenation ultimately results in the formation gaseous hydrocarbons. This consequently increases the overall hydrogen consumption without producing any of the desired liquid hydrocarbons. Rather than inefficiently incorporating hydrogen into these low molecular weight structures, it is possible to reverse the situation, and to utilize them as a source of hydrogen instead [10,11].

The conversion of these water-soluble compounds into hydrogen can be realized by applying catalytic steam reforming. The general approach for this entails water-induced post-pyrolysis phase separation, which essentially fractionates the pyrolysis oil into a lignin-derived water-insoluble oil fraction, and a separate aqueous fraction. However, as a result of this procedure, the aqueous fraction contains not just the light molecular weight monomeric oxygenates, but also significant amounts of 'sugar-type' compounds. These so-called sugars, which originate from the depolymerization of cellulose and hemicellulose, are known to exhibit both limited volatility, and a heavy tendency towards charring and coke formation in catalytic upgrading processes [12–14]. These particular characteristics are highly problematic for steam reforming, and thus high reaction temperatures and steam-to-carbon (S/C) ratios have typically been applied in order to avoid rapid catalyst deactivation in the conversion of aqueous pyrolysis oil feedstocks [15]. In addition to fractionating the already condensed pyrolysis oil, it is possible to incorporate the fractionation procedure into the pyrolysis process itself. By fractionating the pyrolysis oil on the basis of volatility rather than solubility, it is possible to isolate an aqueous fraction containing only a limited amount of thermally unstable sugar-type compounds [16]. It has been recently shown that such a feedstock can be converted to hydrogen by employing relatively mild process conditions [17].

Although the reformability of aqueous pyrolysis oil can be enhanced by fractional condensation as well as other means, catalyst deactivation is still an eventuality that needs to be addressed. One suggested method of alleviating catalyst deactivation is the addition of small amounts of oxygen into the steam reforming process. This technique, which is referred to as oxidative steam reforming (OSR), would in an optimal situation promote the gasification of coke precursors

on the catalyst surface. However, in reality, it is to be expected that the oxygen will also take part in the oxidation of gaseous compounds, e.g. hydrogen and carbon monoxide [18]. In addition to this, the presence of oxygen can also promote homogeneous gas/vapor phase reactions of oxygenate compounds such as alcohols [19,20]. Although these oxidation reactions potentially decrease the yield of hydrogen, their exothermic nature and the consequent heat release helps to meet the energy demands of the endothermic steam reforming reactions [21].

Adding oxygen into a pyrolysis oil steam reforming process has been shown to have a varying influence. Medrano et al. [22,23] observed similar effects in the steam reforming of both acetic acid and an actual pyrolysis oil aqueous fraction over a Ni–Al catalyst in a fluidized bed reactor. Addition of a small amount of oxygen helped to stabilize carbon conversion to gases with acetic acid, and significantly decreased coke formation with the pyrolysis oil aqueous fraction. In both cases, the yield of H₂ decreased only slightly. Czernik and French [18] observed that increasing the amount of oxygen increased carbon conversion to gases while simultaneously decreasing the yield of H₂. Composition of the product gas remained constant for 4 h with four different feedstocks: three whole bio-oils and one aqueous fraction. After 4 h, operation was halted due to pressure buildup in a filter element which was situated between an evaporator and the reforming reactor. In contrast to the more promising findings of the other research groups, Rioche et al. [24] observed a decrease in the H₂ yield and an increase in the rate of catalyst deactivation when adding oxygen. However, the oxygen addition actually reduced carbon deposition, and thus the authors suggested that the reason behind the deactivation could have been sintering of the active Pt metal.

Some steam reforming processes utilize a step called pre-reforming, where heavier and more reactive hydrocarbons are first converted into methane. This is typically carried out at a temperature which is lower than the temperature in the main steam reforming reactor [25]. However, as previously stated, pyrolysis oil oxygenates are more susceptible to steam reforming at higher temperatures, and therefore this kind of conventional low temperature pre-reforming concept would theoretically have only limited usability. Another option would be to utilize a different method of pre-conversion, the objective of which would be to render the pyrolysis oil organics into a more easily steam reformable form, or to alternatively separate some of the compounds which are known to cause catalyst deactivation. One example of the latter approach is using a thermal conversion step prior to the actual steam reforming [26–29]. This essentially leads to the retention of non-volatile compounds in the form of a solid deposit, while the volatile matter passes on to the steam reforming reactor.

The approach that has been adapted in this study employs a combination of pre-conversion and oxidative steam reforming. The pre-conversion step utilizes a zirconia catalyst, which has been developed for the selective oxidation of tars originating from biomass gasification [30]. It was envisioned that utilizing a pre-conversion catalyst which is known to catalyze oxidation reactions could potentially slow down the deactivation of the main steam reforming catalyst. In

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