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Review

Catalytic steam reforming of bio-oil

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ABSTRACT

Hydrogen and synthesis gas can be produced in an environmentally friendly and sustainable way through steam reforming (SR) of bio-oil and this review presents the state-of-the-art of SR of bio-oil and model compounds hereof. The possible reactions, which can occur in the SR process and the influence of operating conditions will be presented along with the catalysts and processes investigated in the literature.

Several catalytic systems with Ni, Ru, or Rh can achieve good performance with respect to initial conversion and yield of hydrogen, but the main problem is that the catalysts are not stable over longer periods of operation (>100 h) due to carbon deposition. Support materials consisting of a mixture of basic oxides and alumina have shown the potential for low carbon formation and promotion with K is beneficial with respect to both activity and carbon formation.

Promising results have been obtained in both fluidized and fixed bed reactors, but the coke formation appears to be less significant in fluidized beds. The addition of O₂ to the system can decrease the coke formation and provide autothermal conditions at the expense of a lower H₂ and CO-yield.

The SR of bio-oil is still in an early stage of development and far from industrial application mainly due the short lifetime of the catalysts, but there are also other aspects of the process which need clarification. Future investigations in SR of bio-oil could be to find a sulfur tolerant and stable catalyst, or to investigate if a prereformer concept, which should be less prone to deactivation by carbon, is suitable for the SR of bio-oil.

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1. Introduction

In the recent decades it has become evident that fossil fuels are a limited resource and that the emission of CO₂ could

cause global warming with severe changes to the climate [1,2]. To diminish the dependency on fossil fuels and to reduce CO₂ emissions much research is focused on new or alternative and sustainable fuels and energy sources. One of the possible

Abbreviations: APR, aqueous phase reforming; DS, desulfurization; GHSV, gas hourly space velocity; LHSV, liquid hourly space velocity; LHV, lower heating value; POX, partial oxidation; SR, steam reforming; SV, space velocity; WGS, water gas shift; WHSV, weight hourly space velocity; Y, yield.

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alternative energy sources is biomass, which is a renewable and CO₂-neutral fuel carbon source. The biomass energy potential has been estimated to be between 50 and 1100 EJ/year in 2050 [3–6] while the total global energy consumption is estimated to be between 600 and 1000 EJ/year in the same year [7]. Based on these numbers it appears that biomass can provide some of the energy needed in the future and hereby delay the depletion of the fossil resources.

Biomass can be converted by thermal and catalytic processes to several types of liquid or gaseous products. It can be gasified to produce synthesis gas, which subsequently can be used to produce power in gas turbines or a wide range of fuels; methanol, DME, alcohols of various chain length by the higher alcohol synthesis, and high grade diesel by the Fischer–Tropsch synthesis [8–10]. Another interesting possibility is to flash pyrolyze the biomass, which produces mainly liquids (bio-oil), and some gases and solids (char) [8,11–13]. The flash pyrolysis is conducted in an inert atmosphere at temperatures between 400 and 600 °C with high heating and cooling rates (1000–10,000 K/s) and low residence time in the reactor (1–2 s). Liquid yields up to 75 wt% can be achieved by a proper choice of operating conditions in the pyrolysis process [8,11,14]. The gas and char yields typically range between 10–20 wt% and 10–15 wt%, respectively [13]. Bio-oil can be produced in several different reactor types ranging from entrained flow to ablative and fluidized bed systems. Demonstration and industrial pyrolysis reactors with capacities between 1 and 50 t/h have been or are in operation [13].

The bio-oil can have a volumetric energy density up to ten times larger than biomass and is therefore more suitable for transport as the transportation cost will be much lower compared with biomass [14]. One of the problems with utilizing biomass in the energy sector can therefore be partly solved by the flash pyrolysis process.

The by-products from the flash pyrolysis can be utilized as the gases can be used to dry the biomass and be combusted to provide energy for the pyrolysis process [8,11]. The char can be combusted as well. However this might be troublesome as the char contains high amounts of inorganics, which can vaporize and condense again on the heat transfer surfaces causing corrosion and reduced heat transfer. Therefore an attractive possibility is to spread the char on agricultural lands as fertilizer and soil improver, which also would sequest CO₂ to some extent [15,16]. According to Lehman and Joseph [16] if 1% of annual plant uptake is converted into char it could mitigate 10% of the anthropogenic CO₂ emissions. The carbon in the char is believed to be released over a period of 1000 years [15]. However, the char could contain PAH's or trace metals which could cause pollution of the soil.

The bio-oil consists of many different oxygenated compounds like acids, ketones, alcohols, phenols, guaiacols etc. The bio-oil and the biomass have similar heating values per mass and the energy efficiency of the pyrolysis is therefore close to the liquid yield in the flash pyrolysis, which means that values around 60–75% can be achieved [17,18]. However, energy should also be supplied to dry, downsize, and pyrolyze the biomass and since the energy from the pyrolysis gases may not be sufficient the energy efficiency for the entire biomass to bio-oil process might be lower.

The distribution among the different types of oxygenates in the bio-oil varies depending on the feedstock and under which conditions the bio-oil was produced. The average oxygenate composition for two bio-oils produced in different reactors and from different feedstock is shown in Table 1. In this table it can be seen that acids and lignin constitutes the largest organic fraction, while significant amounts of water also are present. Acetic acid, hydroxyacetaldehyde, acetol, and levoglucosan constitute some of the most abundant molecules [19].

The physical properties and elemental composition of bio-oil are compared to the composition of fossil fuel oil in Table 2. The fuel oil used for comparison is equivalent to fuel oil no. 4, which is a heavy diesel blend sometimes referred to as residual fuel oil. The most important differences between bio-oil and fuel oil are the oxygen content, sulfur content, and pH. The high oxygen content in the bio-oil induces the low heating value, high acidity, and also instability of the bio-oil as the oxygenates can polymerize under storage. The polymerization causes an increase in viscosity and average molar weight with time [19–21]. A doubling or even tripling of viscosity of bio-oil due to aging might occur over a year [19]. This polymerization might make upgrading of the bio-oil more difficult as complex molecules, which are more difficult to convert, could be formed. Aging of the bio-oil can also decrease the volatility, cause phase separation, and gum formation in the bio-oil as well [20]. Thus long-term storage of the bio-oil could cause severe changes to the bio-oil and should be avoided. The acidity of bio-oil is another problem as corrosive resistant materials are needed for piping and process equipment, which often are more expensive. The sulfur content in bio-oil is much lower than in crude oil which, in general, is advantageous, but even the low levels might be a problem for catalytic processing of the oil especially if Ni or noble metals are used as catalysts.

The bio-oil can be converted to different products and might therefore constitute a platform feedstock in a bio-refinery. It can be converted to a gasoline like product by partial hydrodeoxygenation or to synthesis gas by steam reforming (SR) [8,9,22]. The hydrogen from the SR can be used

Table 1 – The average composition of bio-oil produced through flash pyrolysis of two different types of biomass, a mix of pine and spruce or a softwood mixture in. Pine and spruce bio-oil was produced in a fluidized bed reactor at 460 °C and the bio-oil from softwood was produced in a rotating cone reactor at 500 °C. Results are from a round robin laboratory analysis of the same bio-oils [19]. "Others" include ketones, aldehydes, and alcohols. PAH: Poly aromatic hydrocarbons.

	85% pine and 15% spruce	Softwood mixture
Water [wt%]	20–23	30–35
Acids [wt%]	3–22	3–27
Others [wt%]	2–21	2–27
Sugars [wt%]	4–9	4–7
Phenols [wt%]	3–4	1–3
Lignin [wt%]	2–18	13–32
PAH [ppm]	8	3

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