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Transportation fuels from biomass fast pyrolysis, catalytic hydrodeoxygenation, and catalytic fast hydropyrolysis

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ABSTRACT

This review presents and discusses the progress in combining fast pyrolysis and catalytic hydrodeoxygenation (HDO) to produce liquid fuel from solid, lignocellulosic biomass. Fast pyrolysis of biomass is a well-developed technology for bio-oil production at mass yields up to ~75%, but a high oxygen content of 35–50 wt% strongly limits its potential as transportation fuel. Catalytic HDO can be used to upgrade fast pyrolysis bio-oil, as oxygenates react with hydrogen to produce a stable hydrocarbon fuel and water, which is removed by separation. Research on HDO has been carried out for more than 30 years with increasing intensity over the past decades. Several catalytic systems have been tested, and we conclude that single stage HDO of condensed bio-oil is unsuited for commercial scale bio-oil upgrading, as the coking and polymerization, which occurs upon re-heating of the bio-oil, rapidly deactivates the catalyst and plugs the reactor. Dual or multiple stage HDO has shown more promising results, as the most reactive oxygenates can be stabilized at low temperature prior to deep HDO for full deoxygenation. Catalytic fast hydropyrolysis, which combines fast pyrolysis with catalytic HDO in a single reactor, eliminates the need for reheating condensed bio-oil, lowers side reactions, and produces a stable oil with oxygen content, H/C ratio, and heating value comparable to fossil fuels. We address several challenges, which must be overcome for continuous catalytic fast hydropyrolysis to become commercially viable, with the most urgent issues being: (i) optimization of operating conditions (temperature, H_2 pressure, and residence time) and catalyst formulation to maximize oil yield and minimize cracking, coke formation, and catalyst deactivation, (ii) development of an improved process design and reactor configuration to allow for continuous operation including pressurized biomass feeding, fast entrainment and collection of char, which is catalytically active for side reactions, efficient condensation of the produced oil, and utilization and/or integration of by-products (non-condensable gasses and char), and (iii) long-term tests with respect to catalyst stability and possible pathways for regeneration. By reviewing past and current research from fast pyrolysis and catalytic HDO, we target a discussion of the combined processes, including direct catalytic fast hydropyrolysis. By critically evaluating their potential and challenges, we finally conclude, which future steps are necessary for these processes to become industrially feasible.

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Abbreviations: AC, Activated carbon; ACI, Acid catalyzed reactions; ACP, Phosphorus activated carbon; BFB, Bubbling fluid bed; CAN, Carbonyl number; CFB, Circulating fluid bed; CRA, Cracking; CUS, Coordinatively unsaturated site; daf, Dry ash free basis; db, Dry basis; DCO, Decarboxylation and/or decarbonylation; DDO, Direct deoxygenation; DFT, Density functional theory; DME, Demethylation; DMO, Demethoxylation; DOD, Degree of deoxygenation; EXAFS, Extended X-ray absorption fine structure; FCC, fluid catalytic cracking; GC, Gas chromatography; GHG, Greenhouse gas; GPC, Gel permeation chromatography; HCR, Hydrocracking; HDM, Hydrodemetallization; HDN, Hydrodenitrogenation; HDO, Hydrodeoxygenation; HDS, Hydrodesulfurization; HHV, Higher heating value; HYD, Hydrogenation; IR, Infrared; LCA, Life cycle assessment; LHSV, Liquid hourly space velocity; OECD, Organisation for Economic Co-operation and Development; MS, Mass spectrometry; MT, Methyl transfer; NMR, Nuclear magnetic resonance; ppm, Parts per million; Q-EXAFS, Quick extended X-ray absorption fine structure; SNG, Synthetic natural gas; STM, Scanning tunneling microscopy; TAN, Total acid number; TEM, Transmission electron microscopy; TGA, Thermogravimetric analysis; TOF, Turn over frequency; WHSV, Weight hourly space velocity; XAS, X-ray absorption spectroscopy

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1. Introduction

Today's production and use of energy is responsible for 60% of the global greenhouse gas (GHG) emissions (2016 number) [1]. With an increasing world population and the continued industrialization of developing countries the energy consumption will keep increasing in the near future [2–4]. In addition, the depletion of fossil resources and the wide awareness of anthropogenic global warming have intensified the search for renewable and sustainable energy resources that can support our modern way of living [5].

The increase in the anthropogenic CO_2 emissions can be traced back to the industrialization that accelerated through the 20th century [5]. In 2010, CO_2 released from fossil fuels and industrial processes constituted 65% of anthropogenic GHGs emitted [5]. Regarding the total GHG emissions, the transport sector contributed to 14% with the energy supply sector covering 35%, industry 21%, agriculture and forestry 24%, and buildings 6%, respectively [5]. In 2016, 20% of the human population still lived outside the electrical grid and around 40% relied on wood, coal, or animal waste for cooking and heating [1]. This is expected to change and, hence, as projected by the U.S. Energy Administration in 2016, the global energy consumption of non-OECD countries will increase significantly from $330 \cdot 10^6$ TJ in 2012 to $560 \cdot 10^6$ TJ in 2040 (see Fig. 1a) [4].

In 2011, The World Bank estimated that there were 176 vehicles per 1000 people on average in the world. The number was 55 for low and middle income countries, 620 for high income countries, and 797 in the U.S. alone [6]. Especially for non-OECD countries, the liquid fuel consumption is expected to increase (see Fig. 1b) [4]. In order to accommodate the increasing demand from developing countries it is crucial to develop technologies for a sustainable production of renewable transportation fuels. Fluctuations in the crude oil prices [4,7], which in 2016 were historically low [7], affect the economy of emerging technologies immensely.

Today, the infrastructure of the modern society is almost solely based on carbon based fuels due to their very high energy density and their availability from the still large oil reserve. At the same time, wind and solar based electricity production is reaching a mature stage and is today cost competitive with the fossil based in some regions of the world [8]. The major threshold for both fuel-cell and battery driven vehicles is the necessity to build a new fuel infrastructure with charging stations for H_2 or electricity, respectively [9]. Battery driven vehicles also struggle with a low energy density and instability of the currently dominant lithium batteries [9]. Another obstacle lies in the availability of wind and solar based electricity and lack of good storage technologies, e.g. chemical energy storage via hydrogen is not yet economically feasible [10]. Electricity production from photovoltaic cells peaks during the day, whereas power consumption typically peaks in the morning and afternoon, which results in the so-called duck-curve [11]. Consequently, carbon based fuels currently appear as an attractive candidate for the principal part of the transportation energy, and biomass appears as the most promising renewable source. Additionally, for aviation, heavy duty road transport, and shipping industries, it is unlikely that these will be fueled by electricity in the near future. The earth's biomass production capacity can however not be increased to cover the total global energy demand [12], and it is important to stress that the future energy supply system is most likely to be based on several synergetic technologies, which can complement each other, for example in order to fill the gap in the duck-curve.