Continuous hydrodeoxygenation of liquid phase pyrolysis oil with biogenous hydrogen enriched synthesis gas for fuel production

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1. Introduction and Short Description:

Science is racing against time to stop global warming. Since the Kyoto protocol [1], published in the mid-90s, climate policy was set in motion. Different protocols, the most common ones being the Paris agreement [2] in 2015 and the renewable energy directive [3] (RED) in 2009 of the European Union with a recast in 2018 [4], have evolved. According to the Paris agreement, the climate change is to hold significantly below 2°C. Experts are not sure if this goal is still achievable. [5] In all agreements it is clearly stated, that significant reduction of GHGs has to occur in order to achieve CO_2 neutrality eventually. This ambitious goal can only be achieved if all feasible sources for renewable energy production are exploited.

From this point of view, the concept of biofuel production via the bioCRACK process and subsequent hydrodeoxygenation (HDO) of liquid phase pyrolysis (LPP) oil with synthesis gas (syngas) from renewable feed has been developed (Figure 1).

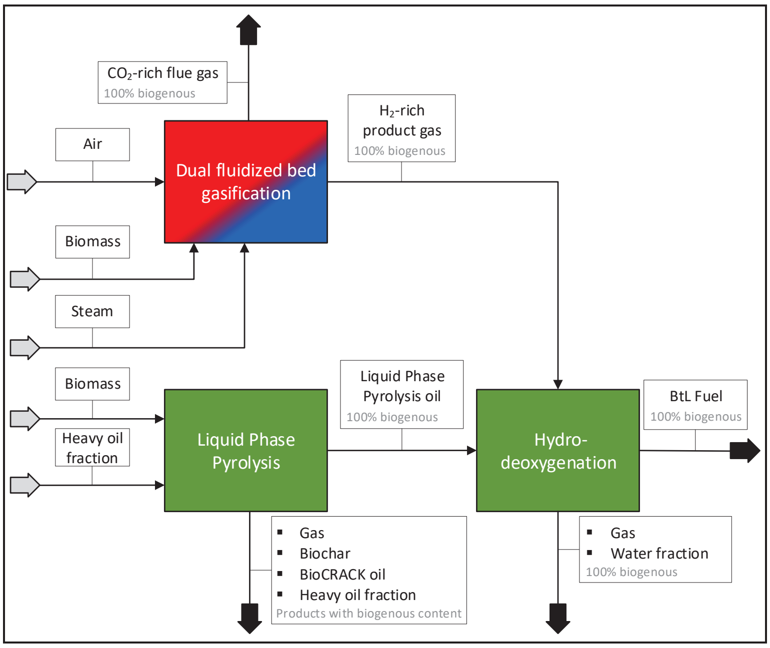

Figure 1: Combined biofuel production route

It combines two major pathways for biomass liquefaction: indirect liquefaction through gasification [6] with subsequent synthesis and direct liquefaction through pyrolysis [7] and HDO.

In the **bioCRACK process** [8], biomass is liquefied through pyrolysis in a heavy oil refinery stream; whereas non-polar biomass fragments are then dissolved in the heat carrier oil and polar biomass constituents build up LPP oil together with the water of reaction. The heat carrier oil, which is also partly cracked during this process, is afterwards upgraded in existing refinery units. LPP oil needs a more extensive upgrade such as HDO.

In order to replace fossil hydrogen and prevent extensive gas cleaning concepts, LPP oil was subsequently hydrotreated with a hydrogen rich synthesis gas, produced via **sorption enhanced reforming (SER)** [9]**,** by making use of the water-gas shift (WGS) reaction. The combined biofuel production concept of LPP and SER is shown in Figure 1.

2. Process design and methodology

Liquid phase pyrolysis was performed in the bioCRACK pilot plant, which was designed for a maximum throughput of 100 kg/h biomass.
Gasification was carried out in a 100 kW_{th} **dual fluidized bed (DFB) steam gasification reactor** in technical scale.
The HDO experiments were performed in a lab scale plug flow reactor with a throughput of 10 g/h LPP oil, equivalent to a liquid hourly space velocity of 0.5 h^{-1}, at 350°C and 120 bar. The reaction was catalyzed heterogeneously with a sulfided metal oxide catalyst.

3. Results and Discussion

For HDO, a test gas bomb with the composition of the SER produced syngas, as shown in Table 1, was used.

Table 1: Composition of the syngas test gas bomb

Product gas composition		Test gas bomb
H_2	[vol%$_{db}$]	70.5
CO	[vol%$_{db}$]	8
CO_2	[vol%$_{db}$]	5.5
CH_4	[vol%$_{db}$]	14
C_2H_4	[vol%$_{db}$]	1
C_2H_6	[vol%$_{db}$]	1

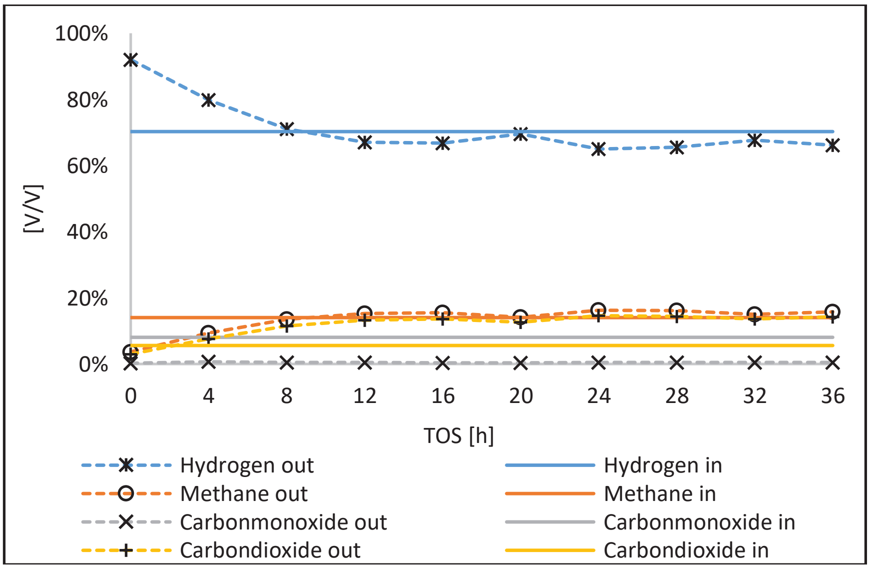

Figure 2: Gas phase composition of HDO inlet (syngas) and outlet gas

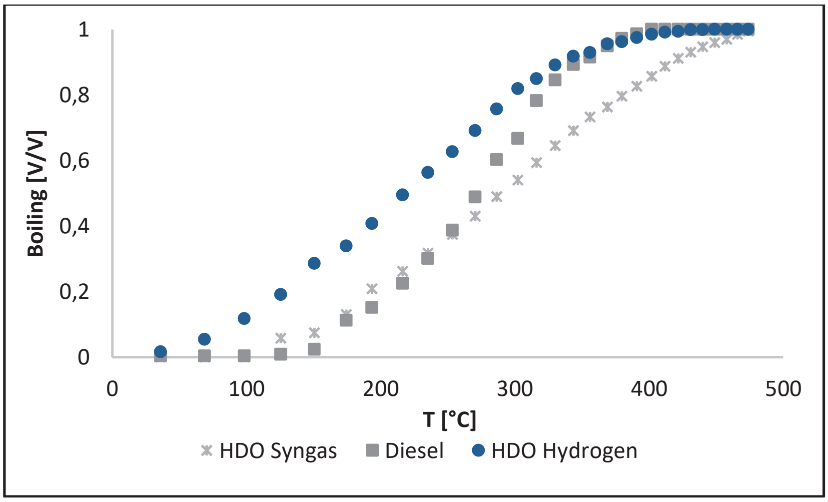

Figure 3: Boiling range of the HDO syngas product compared to HDO with pure hydrogen as well as diesel

In Figure 2, the composition of the HDO inlet gas phase is compared with the HDO outlet gas phase. In the first 8 hours, pure hydrogen, which was used for sulfidation, was replaced by syngas. Afterwards, a stable outlet gas phase composition was achieved. CO was nearly fully converted into CO_2 with a stoichiometric factor of one, Methane was not converted. The net hydrogen content decreased slightly

Thus, a product with close to diesel properties, comparable to HDO with pure hydrogen, was produced, which reflects in the boiling range in Figure 3.

Literature

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