Hydrothermal liquefaction of Dried Distillers Grains with Solubles

Anders Juul Mørup\textsuperscript{a1}, Per Runge Christensen\textsuperscript{a2}, Bo Brummerstedt Iversen\textsuperscript{a*}

\textsuperscript{a} Center for Energy Materials, Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C.

Hydrothermal liquefaction (HTL) is a novel biofuel process in which superheated water is utilized to liquefy second-generation biomass into crude bio-oil. The bio-oil is water insoluble and can be mechanically isolated from the process water.

HTL is performed in the range of 280-380 °C and 70-300 bar and utilizes the unique properties of hydrothermal water. The self-dissociation of water increases from $10^{-14}$ at room temperature to $10^{-11}$ at 250 °C, 250 bar and causes subcritical water to catalyse acidic and basic reactions. Above the critical temperature, $T_c=374.4$ °C, the self-dissociation is inhibited because water loses the polarity needed to solvate $\text{H}_3\text{O}^+$ and $\text{OH}^-$, and free radical reactions instead dominate the reaction chemistry. In addition, the polarity of water is also highly temperature dependent. Supercritical water has a dielectric constant of approximately 1 and dissolves nonpolar and hydrophobic substances such as HTL bio-oil. Hence water functions both as a catalyst and solvent in the HTL process.

The HTL process is very robust in the sense that it can accept many types of biomass, such as algae, wood or even waste biomass like municipal waste, industrial by-products or manure. The biomass utilized in this study is Distillers Dried Grains with Solubles (DDGS), which is a by-product of the corn-based bioethanol fermentation process.

In order to study the effect of reaction temperature, hydrothermal liquefaction experiments of DDGS were conducted over a range of temperatures. This was done using a novel stop-flow reactor system, which enables extensive control of the process parameters and rapid heating of the biomass feed, plus the possibility of conducting multiple experiments sequentially. These unique features helped achieve highly reproducible oil yields in the subcritical temperature range.

The experiments were carried out at a pressure of 250 bar and a residence time of 15 minutes, while varying the temperature from 300-400 °C. DDGS was successfully converted into a pourable crude oil. The bio-oil samples were characterized in terms of oil yield, elemental composition, and higher heating value (HHV).

The increase in temperature from 300-360 °C resulted in an increase of the oil from 17.0-26.6 wt%, while additionally reducing solid residue formation. Increasing the temperature to 400 °C, the oil yield increased to 49.6 wt% while reducing char formation further.

When DDGS is subjected to the HTL process, the carbon and hydrogen content increases from 43.8-73.7 wt% and 6.8-9.1 wt%, respectively. In addition, the oxygen content is observed to decrease from 35 wt% to a minimum of 10 wt% at 400 °C. The sulfur and nitrogen content of the bio-oils are slightly lower than that of the DDGS, but is not affected by increasing reaction temperatures.

The CHNOS data is used to calculate the HHV of DDGS and bio-oil. The heating value of the bio-oil increases with reaction temperature, as expected from the decrease in heteroatom concentration. At 400 °C the bio-oil obtains the highest HHV of 36 MJ/kg. Compared to conventional fuels, the HHV of the bio-oil is in between that of diesel and coal.

In summary, higher reaction temperatures resulted in improved oil yields, less char formation and enhanced HHV of the oil. A reaction temperature of 400 °C was found to produce bio-oil in the highest yields and of the best quality.

\textsuperscript{a*}Corresponding author: bo@chem.au.dk
\textsuperscript{1}andersjm@chem.au.dk
\textsuperscript{2}per@chem.au.dk