

Bio-oil and bio-char from low temperature pyrolysis of spent grains using activated alumina

The pyrolysis of spent grains resulting from bio-ethanol and beer production was investigated at temperatures between 460 and 540°C using an activated alumina bed. The results showed that the bio-oil yield and quality depend principally on the applied temperature where pyrolysis at 460°C leaves a bio-oil with lower nitrogen content in comparison with the original spent grains and low oxygen content. Overall, value can be added to the spent grains opening a new market in bio-fuel production without the needs of external energy.

Spent grains are the main by-product of the bio-ethanol production process and the bio-ethanol industry is currently exploiting new ways to maximize its margin by further recovery of either energy or co-products from the spent grains, which currently are partially used as animal feed additive. This work describes an alternative means of releasing energy from the spent grains (Figure 1) using thermo-chemical conversion to convert the spent grains into a low-oxygen containing bio-oil and high nitrogen containing bio-char using an alumina catalyst. Using this approach, catalytic pyrolysis can convert the spent grains into a bio-oil suitable for upgrading into transportation fuels and a bio-char where the nitrogen, phosphorus and alkaline metals are concentrated in sequestered carbon.

The pyrolysis-bio-oil is a very complex mixture of oxygenated aliphatic and aromatic hydrocarbons and the key to large scale use of pyrolysis oil is therefore the removal of oxygen to facilitate its further conversion into industrial commodity chemical feedstocks. In addition to bio-oil, bio-char is attracting growing attention as a valuable by-product since it is able to sequester carbon and may be used as a soil amendment.

The experimental devices used in this work (Figure 2) principally consisted of a pressurized injection system, a sample chamber, a fluidized bed reactor, an electrical heater and a tar trap. The gases were analyzed using a Hiden Analytical HPR-20 QIC MS with 200 amu mass range capability to evaluate the content of CO₂, H₂ and CH₄ and equipped with a HAL-RC quadrupole mass spectrometer. The Flow Control Inlet ensured stable mass spectrometer operation through a sample pressure range from 200mbar to 2bar. A fast sampling Quartz Inlet Capillary (QIC) was used to sample the gas from the gas-bag at 1bar. The scan range used was between 1 and 200amu and the scan speed was of the order of 10,000 amu/sec. Pure carbon dioxide and nitrogen were used to calibrate the instrument.

The bio-oil from spent grains could meet about 9% of the renewable obligation in the UK. Also, the bio-char contains about 20% of original nitrogen (Table 1) resulting in a very attractive product for soil amendment and carbon sequestration.

	wt %				
	460°C	490°C	520°C	540°C	
<i>Table 1</i> Effect of temperature on total nitrogen distribution in the starting spent grains, into bio-oils and bio-chars for spent grains from wheat (WSG) and barley (BSG).	WSG (Original)	100.0	100.0	100.0	100.0
	WSG bio-oil	61.3	62.0	71.5	54.5
	WSG bio-char	19.2	18.5	16.5	16.0
	BSG (Original)	100.0	100.0	100.0	100.0
	BSG bio-oil	67.6	81.2	82.1	57.5
	BSG bio-char	18.0	18.7	15.7	13.3

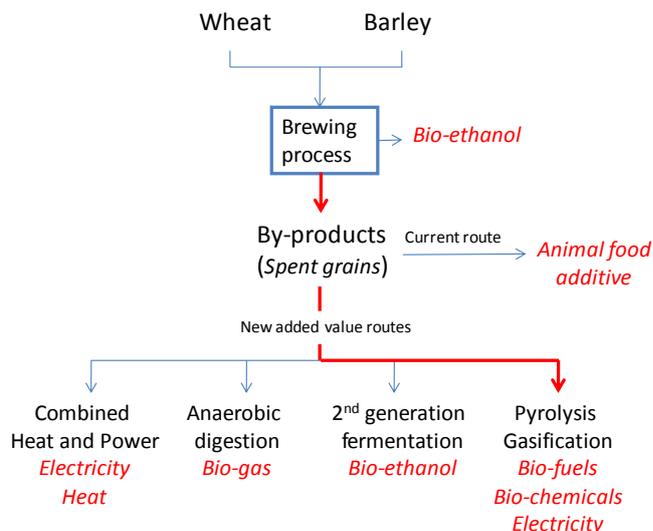


Figure 1 Routes for refining bio-ethanol by-products into bio-gas, bio-ethanol, liquid biofuels or directly electricity and heat.



Figure 2 Fluidised Bed Reactor used for the spent grains pyrolysis.

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