Department of Chemical Engineering

DBD plasma microbubble reactor for pre-treatment of lignocellulosic biomass

A. Wright* [a], H. Bandulasena [a], A. Shaw [b], F. Iza [b], D. Leak [c]

[a] Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire, LE 11 3TU, United Kingdom
[b] School of Electronic, Electrical and Systems Engineering, Loughborough University, Loughborough, Leicestershire, LE 11 3TU, United Kingdom
[c] Department of Biology and Biochemistry, University of Bath, BA2 7AY, United Kingdom

Loughborough University

Motivation: To investigate the effectiveness of pretreatment of lignocellulosic biomass with the highly oxidative species produced by a dielectric barrier discharge (DBD) plasma. The plasma is formed at the gas-liquid interface of a microbubble; facilitating the high mass transfer of unstable oxidative species immediately after production. For effective dispersion microbubbles were generated by the conjunction of a fluidic oscillator and a microporous nickel membrane.

EXPERIMENTAL SET-UP

The aim of the project is to develop and characterize a plasma-microbubble reactor for the pre-treatment of biomass samples to break down lignin to aid fermentation of cellulose and hemi cellulose for the production of bioethanol [1]. Miscanthus was used as it is grown as a dedicated biomass crop in the UK. It is indigestible by humans and does not compete with land for food crops such as corn or maize.

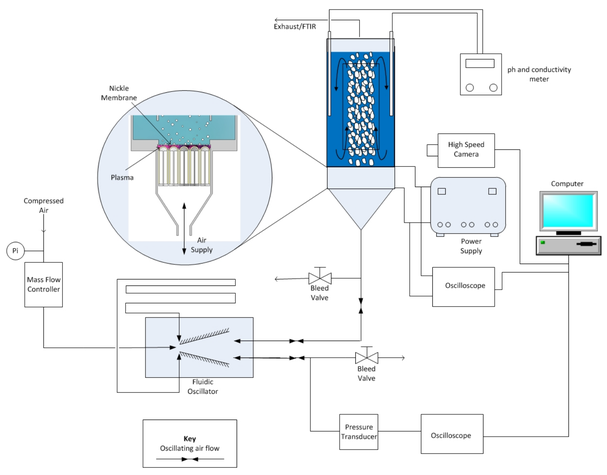


Figure 1: The experimental rig has compressed air feed to a fluidic oscillator (FO) which creates an oscillating air source [2]. This then passes through a plasma modules which produces highly reactive species. The species are formed at the gas liquid interface whilst simultaneously being trapped in microbubbles produced by the FO. The microbubbles then allow high mass transfer to the miscanthus.

CHARACTERIZATION WITHOUT LIQUID

The plasma was driven at 19kHz and 10kVrms and modulation was used to control the operation temperature. The duty cycle of the modulating signal was varied between 10% and 45% by adjusting the on-time between 90 and 663ms and keeping a constant off-time of 810 ms. Duty cycles of 5%, 10% ,15% and 45% were tested with O_3 and NO_x products measured by Fourier transform infrared spectroscopy (FTIR).

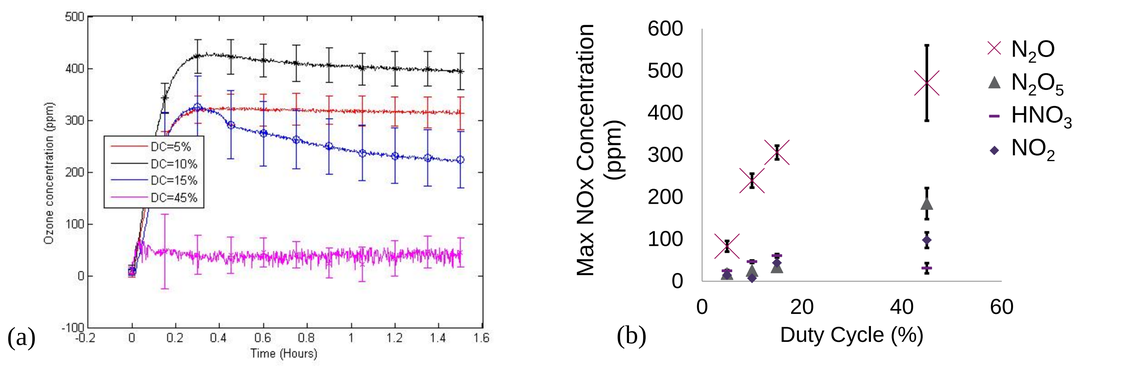
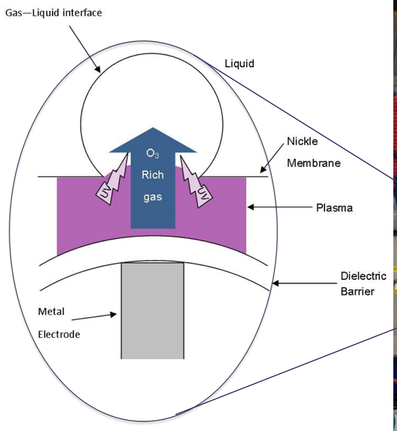


Figure 3: (a) shows the best conditions for ozone production is at 10% duty cycle. (b) shows that NO_x production increases with the duty cycle.

NOVELTY

The novel part of the project is bringing the plasma to the gas-liquid interface enhancing the transfer of species into the liquid phase by encapsulation in microbubbles. Proximity of production combined with the microbubbles ensure high mass transfer for efficient breakdown of biomass [3].



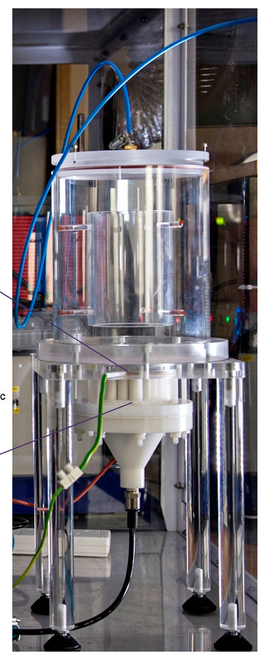


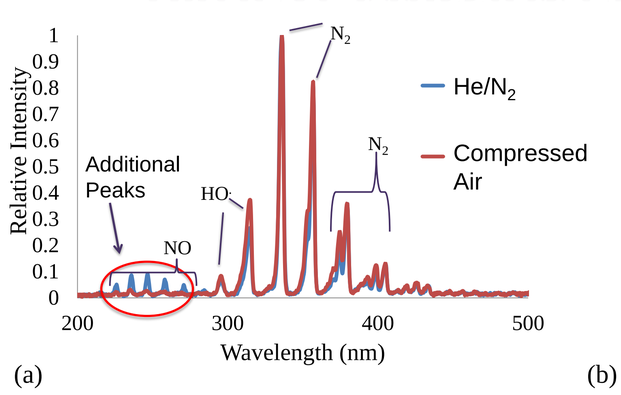
Figure 2: A schematic diagram of the DBD plasma at the gas-liquid interface. Ozone, other highly reactive species and UV light are produced in situ at the microbubble interface making the transfer of short-lived species possible.

Table 1: Products of the plasma

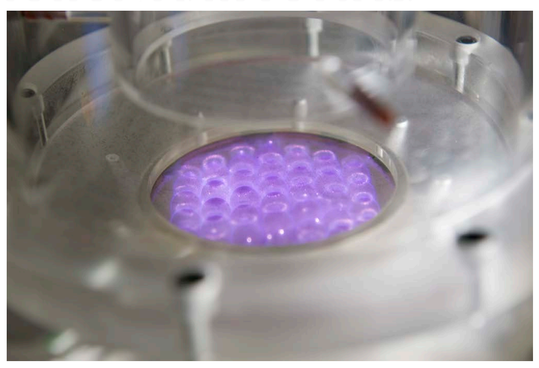
Species	F_2	·OH	O	O_3	H_2O_2	HO_2	Cl_2	HNO_3	NO_2	H_2	O_2^-	$ONOO^-$	NO
Redox Potential (v)	3.03	2.80	2.42	2.07	1.78	1.70	1.36	0.96	0.46	0	-0.33	N/A	-0.96
Produced in this study	N	Y	Y	Y	Y	Y	N	Y	Y	N	Y	Y	Y

Table 1 gives a list of species formed from the plasma with the addition of reference voltages [4].

OPTICAL EMISSION CHARACTERIZATION



(a)



(b)

Figure 3: (a) spectrum produced by the plasma for compressed air and a 5% He/ 95% N_2 mixture. (b) visual appearance of the plasma with He/N_2 mixture.

It was found that compressed air produced emissions in UVA (400 nm-315 nm) and UVB (315 nm-280 nm) range, but did not produce UVC (280 nm-100 nm). A gas mixture containing 5% He in N_2 produced UVC in addition to UVA and UVB as shown in fig 3 [5]. This is due to the formation of NO resulting from the reactions of ozone with metastable N_2 in addition to atomic nitrogen reacting with atomic oxygen and OH radicals.

CHARACTERIZATION WITH LIQUID

FTIR spectroscopic analysis of exhaust gases can only be detect long lived species. For short lived species such as ·OH, a chemical probe that reacts with the radicals yielding a fluorescent product (terephthalic acid) was used and the rate of change of the chemical probe can be used to infer ·OH production (see fig 4). Indigo, a widely used probe, was also used to measure the level of oxidative species produced by the reactor in the liquid phase at different duty cycles. As the die is broken down by oxidative species such as ozone the absorption band at 600nm diminishes and the rate of change measured.

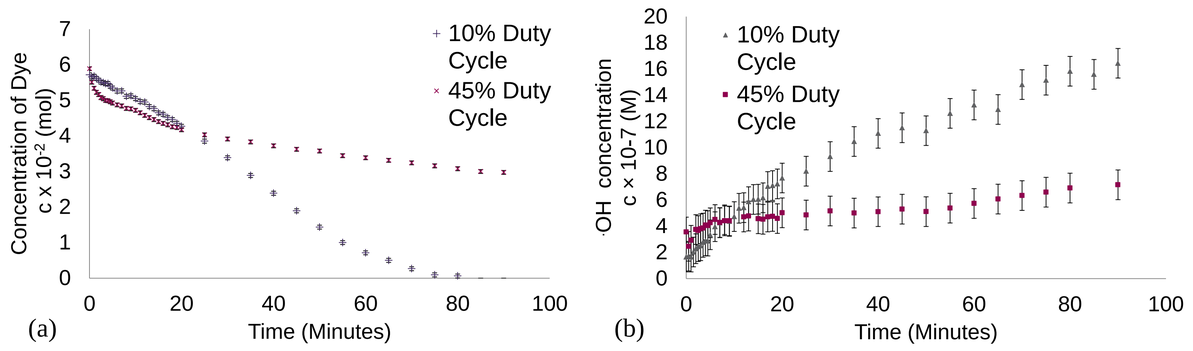


Figure 4: (a) The rate of change of the indigo die (b) ·OH concentration measured using the following reaction $C_6H_4(COOH)_2 + \cdot OH \rightarrow C_6H_4(COOH)_2OH$ [6].

Terephthalic acid concentration was measured by fluorescence spectroscopy. It can be seen that 10% duty cycle produces more 2-hydroxy terephthalic acid and results in faster destruction of indigo, making this the preferred operation condition for the plasma system ·OH production. Conductivity and pH were also measured with the results in fig 5.

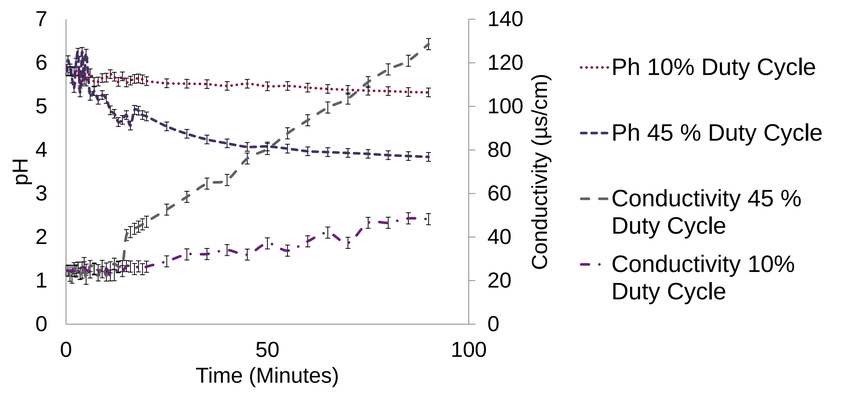


Figure 5: The distilled water becomes more acidic and conductive at 45% duty cycle due to the higher levels of NOx produce.

CONCLUSION

A DBD plasma-microbubble reactor has been devolved and characterized. Two operating regimes have been identified. 10% duty cycle was favourable for O_3 and ·OH production as long 'off' times aid sufficient cooling. 45% duty cycle produced more NO_x compared to lower duty cycles. Both regimes are currently being trialled on miscanthus to determine the best operating conditions for lignin break down. The He/N_2 mixture produces UV in the short wavelength range (~254 nm) in addition to the longer wavelengths produced by compressed air only. Further work is being done to coat the surface of the membrane with TiO_2 to increase ·OH production and improve efficiency. Two new reactors with active cooling are also under development. It is hoped this will enable the reactor to run at higher duty cycles at lower temperatures hence producing more ozone.

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CONTACT INFORMATION

Department of Chemical Engineering
Loughborough University
Leicestershire LE11 3TU, UK
A.wright-14@student.lboro.ac.uk
www.lboro.ac.uk/departments/chemical