

## Pre-treatment of lignocellulosic biomass using a novel hydrodynamic cavitation reactor for enhancing biogas production

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### Highlights

- Used vortex diode as a cavitation reactor to pre-treat lignocellulosic biomass.
- Measured bio-methanation capacity for a range of cavitating conditions.
- Developed guidelines to optimise pre-treatment for maximising biogas production.

### 1. Introduction

Biogas production via anaerobic digestion (AD) is one of the oldest known technologies which is being used till date for the treatment of sewage and other waste water streams [1]. Organic substrates in the waste are excellent feedstocks for biogas production. Amongst the variety of substrates that are compatible for AD such as vegetable/fruit wastes, waste water, municipal solid waste and agricultural wastes [2-5], agricultural wastes such as grass and silage present a viable class of feedstock from a Northern Ireland point of view. In this work, we use recently disclosed novel cavitation reactor (vortex diode) to pre-treat lignocellulosic biomass (LCB) to make it more digestible in AD [5].

A number of factors such as pH, temperature, residence time, carbon to nitrogen ratio, type of substrates, particle size and composition of the inoculum can affect the overall biogas production process [1, 6]. Amongst the abovementioned factors, the type of substrate plays a key role in determining the overall biogas yield. In context with grass and silage as feedstock for biogas production in the current work, cellulose and hemicellulose present in this lignocellulosic biomass (LCB) are the digestible fractions for AD. The crosslinking between lignin, cellulose and hemicellulose present in the LCB matrix makes it difficult to access the digestible fractions. To supply the inoculum with the digestible fractions, recalcitrant lignin present in LCB must be degraded partially to release cellulose and hemicellulose.

Current pretreatment methods to degrade lignin in LCB include physical treatment, steam explosion, liquid hot water treatment, acid/alkali treatment, ammonia explosion, ionic liquid treatment and lignolytic enzymatic/biological treatment [7]. These methods mentioned are expensive, environmentally unfavourable, slow or energy intensive. An alternative to these methods is hydrodynamic cavitation (HC) which is used in this work to pretreat LCB to release cellulose and hemicellulose. Cavitation is the phenomenon of formation, growth and collapse of bubbles (cavities). Collapsing cavities lead to intense shear and localised very high temperature (~5000 K) and high pressures (~1000 atm). The high pressure and temperature generated by cavity collapse leads to formation of OH radicals. Intense shear as well as OH radicals cause degradation of lignin matrix and opens up cellulose and hemicellulose. [8, 9].

The aim of this work is to harness HC for the pretreatment of LCB by degrading lignin and enhancing biogas production. Unlike the conventional cavitation devices like venturi or orifice [8, 9], we use vortex diode which uses rotational flow for generating cavitation. Vortex diodes do not contain any moving parts and do not use small constrictions which reduces maintenance requirements and risk of clogging.

### 2. Methods

#### 2.1 Materials and characterization:

Grass and silage were used as feedstock for the experiments. The LCB was used with or without any milling. The total solids, volatile solids, moisture and ash content of the feedstock and the HC pretreated solids were

analysed. Fourier transform infra-red spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetry (TGA) and scanning electron microscopy (SEM) analysis of the total solids was performed before and after the HC pretreatment. Coumarin was used as the probe molecule to determine the OH radical quantities produced by the HC set up under various operating inlet pressures.

## 2.2 HC Experiment:

A bench scale hydrodynamic cavitation device with 1 m<sup>3</sup>/hr nominal flow rate of vortex diode (Fig. 1) was set-up. The LCB pre-treatment was carried out at different pressure drop values across the cavitation reactor. Generation of OH radicals was quantified by measuring 7-hydroxycoumain, using a fluorescent spectrometer. Biomethanation potential of pre-treated LCB was measured by collecting the biogas in tedler bags and analysing its composition using a GC-FID (gas chromatograph equipped with a flame ionization detector). Based on the biomethanation potential, optimum conditions for LCB pretreatment was identified. Guidelines for optimising the pre-treatment of LCB were developed.

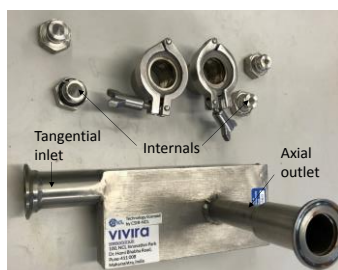


Figure 1. Vortex diode as a cavitation reactor.

## 3. Results, discussion and conclusions

Cavitation performance of vortex diode was first quantified using coumarin, with water as a medium (in absence of LCB). Conditions for cavitation inception and choking cavitation were identified. Generation of OH radicals is expected to exhibit non-monotonic relationship with pressure drop across the diode. Quantitative data on this was obtained. Systematic pre-treatment experiments were carried out at varying loading of LCB in water and its influence on cavitation characteristics was studied. Comprehensive physical and chemical analysis of pre-treated LCB was carried out as detailed in section 2.1. Useful relationships among cavitation conditions, physico-chemical analysis and measured biomethanation potential were developed and verified. OH radical quantification was useful to determine the optimized conditions required for the HC of LCB. Efforts were made to use cavity dynamics model to understand the observed relationships. Based on the experimental and computational results, appropriate guidelines were developed to optimise pre-treatment of LCB using vortex diode as a cavitation reactor. The approach and results presented here is useful for developing an effective pre-treatment method for LCB which can be easily scaled-up.

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## Keywords

Biogas, lignocellulosic biomass, hydrodynamic cavitation, vortex diode.

## Short CV to be considered for the “Gianni Astarita Young Investigator Award”

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### Education

PhD (Chemical Engineering) – Queen’s University Belfast, UK – 2017

M.SC (Environmental Engineering) – National University of Singapore, Singapore – 2010

B.Tech (Biotechnology) – KVCET, affiliated to Anna University, Chennai, India – 2009

### Research experience

1. Research fellow – Queen’s University Belfast

Working on the hydrodynamic cavitation pretreatment of lignocellulosic biomass for the production of biogas via anaerobic digestion

2. Post-doctoral research associate – Birmingham City University (6 months)

Worked on the design and optimisation of a counter flow leach bed reactor (pre-digester) for the production of biogas from food waste.

3. PhD student – Queen’s University Belfast (3 years)

Worked on the development of photocatalytic reactor technology for the production of fermentable sugars.

4. Research Engineer – National University of Singapore (2.5 years)

Worked on photoelectrochemical water splitting for the production of value added chemicals (Biofuels), an updated comprehensive techno-economic analysis of algae biodiesel and abundance and diversity of methanogens, methanotrophs and ammonia oxidizing archaea in Singapore mangroves.

### List of publications

1. Nagarajan, S., Lawton, L. A., Irvine, J. T. S., and Robertson, P. K. J\*. (2017). “Photocatalytic Fermentable Sugar Production from Native and Regenerated Cellulose – A Comparison” to be submitted to Green Chemistry journal.
2. Nagarajan, S., McCurdy, C., Lawton, L. A., Irvine, J. T. S., and Robertson, P. K. J\*. (2017). “Photocatalytic Fermentable Sugar Production in a Stacked Frame Photocatalytic Reactor” to be submitted to Energy and Environmental Science journal.
3. Wu, C., Nagarajan, S., Li Jie, H., Siva, V., Sun, Z and Zhou, Z\*. (2016). “Bioelectrocatalyzed reduction of carbon dioxide by pure culture of *Methanobacterium thermoautotrophicum* in single-chamber microbial electrolysis cells.” submitted to the Applied Energy Journal (under review).
4. Nagarajan, S\*, Skillen, N. C., Lawton, L. A., Irvine, J. T. S., and Robertson, P. K. J\*. (2017). “Cellulose II as bioethanol feedstock and its advantages over native cellulose.” Renewable and Sustainable Energy Reviews journal, <https://doi.org/10.1016/j.rser.2017.03.118>
5. Nagarajan, S\*, Stella, L., Lawton, L. A., Irvine, J. T. S., and Robertson, P. K. J\*. (2017). “Mixing Regime Simulation and Cellulose Particle Tracing in a Stacked Frame Photocatalytic Reactor.” Chemical Engineering Journal, <http://dx.doi.org/10.1016/j.cej.2016.12.016>
6. Nagarajan, S\*, Skillen, N. C., Fina, F., Zhang, G., Randhorn, C., Lawton, L. A., Irvine, J. T. S., and Robertson, P. K. J\*. (2017). “Comparative assessment of visible light and UV active photocatalysts



by hydroxyl radical quantification.” *Journal of Photochemistry and Photobiology A: Chemistry*, <http://dx.doi.org/10.1016/j.jphotochem.2016.10.034>

- This article was featured in Newsrx’s Nanotechnology Weekly magazine dated 23-Jan-2017.

- This paper was the 9th most downloaded article from the journal between April – July, 2017.

7. Jing, H\*, Cheung, S., Zhou, Z., Wu, C., Nagarajan, S and Liu, H. (2016). “Spatial variations of the methanogenic communities in the sediments of tropical mangroves”. *PLoS ONE*, <http://dx.doi.org/10.1371/journal.pone.0161065>
8. Jing, H\*, Xia, X., Liu, H., Zhou, Z., Wu, C., and Nagarajan, S. (2015). “Anthropogenic impact on diazotrophic diversity in the mangrove rhizosphere revealed by nifH pyrosequencing”. *Frontiers in Microbiology*, <http://dx.doi.org/10.3389/fmicb.2015.01172>
9. Nagarajan, S., Chou, S. K., Cao, S., Wu, C., and Zhou, Z\*. (2013). “An Updated Comprehensive Techno-Economic Analysis of Algae Biodiesel.” *Bioresource Technology*, <http://dx.doi.org/10.1016/j.biortech.2012.11.108>

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### Role as a reviewer

Reviewed papers for *International Journal of Green Energy*, *Applied Energy*, *PLoS ONE*, *The Journal of Physical Chemistry* and *Journal of Environmental Biology*.

### Talks/Lectures

1. Invited Keynote Speaker for the International Conference on Application of Green Technology in Engineering and Applied Sciences (ICGTEAS 2013), held in Adiparasakthi Engineering College, Melmaruvathur, Chennai, INDIA from 29-Mar-2013 to 30-Mar-2013.
2. Speaker at the autumn 2016 UK & ISPC network meeting held at University College London on 14th September, 2016 on the title “Development of a photocatalytic reactor for the production of fermentable sugars”.
3. Speaker at the autumn 2015 UK & ISPC network meeting held at Queen’s University Belfast on 9th September, 2015 on the title “Quantification of OH radicals on novel photocatalysts”.

### Awards/Honours

1. PhD studentship and full fee scholarship awarded for the 1st year PhD by Robert Gordon University, Aberdeen, Scotland, UK.
2. PhD studentship and full fee scholarship awarded for the 2nd and 3rd year PhD by Queen’s University Belfast, Belfast, Northern Ireland, UK.
3. Travel grant awarded by IChemE to attend the IChemE Biochemical Engineering Young Researchers’ Meeting 2016 in Dublin.
4. Won five 1st places, three 2nd places and one 3rd place for paper and poster presentation in various national level technical symposia and conferences in India between 2006 and 2009.
  - Topics include biodegradation and biosorption of various dyes and bioethanol production from waste paper and vegetable wastes.

### Professional memberships

1. A member of the UK Anaerobic digestion network (Apr’17-till date)
2. An associate member of the Royal Society of Chemistry (Sep’15-till date).
3. A member of the European Federation of Biotechnology (Oct ’08-till date).
4. A member of the Bioenergy Society of Singapore (18-Jun-12 to 17-Jun-13).