ENERGETICALLY EFFICIENT COMBINATIVE PRETREATMENT OF MARINE MACROALGAL BIOMASS FOR BIOMETHANE PRODUCTION: EXPERIMENTAL STUDIES, KINETICS AND BIODEGRADABILITY MODELLING

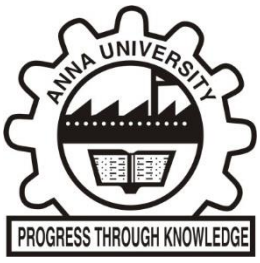
A THESIS

Submitted by

TAMILARASAN K

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY



FACULTY OF CIVIL ENGINEERING

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CERTIFICATE

This is to certify that all corrections and suggestions pointed out by the Indian /Foreign Examiner(s) are incorporated in the Thesis titled " Energetically efficient combinative pretreatment of marine macroalgal biomass for biomethane production: experimental studies, kinetics and biodegradability modelling " submitted by Mr. Tamilarasan.K

J. Rajesh

Signature of the Supervisor

Place : Tirunelveli

Date : 12/4/19

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Proceedings of the Ph.D. Viva-Voce Examination of Mr.Tamilarasan.K held at 11:00 AM on 12.04.2019 in Conference Hall Anna University Regional Campus - Tirunelveli

The Ph.D. Viva-Voce Examination of Mr.Tamilarasan.K (Reg. No. 1612189105) on his/her Ph.D. Thesis Entitled " Energetically efficient combinative pretreatment of marine macroalgal biomass for biomethane production: experimental studies, kinetics and biodegradability modelling " was conducted on **12.04.2019** at 11:00 AM in the Conference Hall Anna University Regional Campus - Tirunelveli.

The following Members of the Oral Examination Board were present:

1. Dr. P.Sivashanmugam,Professor,Department of Chemical Engineering,National Institute of Technology ,Tiruchirappalli-620015 — Indian Examiner
2. Dr. S.T.Ramesh,Professor,Department of Civil Engineering,National Institute of Technology ,Tiruchirappalli 620015 — Subject Expert
3. Dr. Rajesh Banu.J,Assistant Professor, Department of Civil Engineering, Anna University, Regional Centre,Tirunelveli — Supervisor

The research scholar, Mr. Tamilarasan.K presented the salient features of his/~~her~~ Ph.D. work. This was followed by questions from the board members. The questions raised by the Foreign and Indian Examiners were also put to the scholar. The scholar answered the questions to the full satisfaction of the board members.

The corrections suggested by the Indian/Foreign examiner have been carried out and incorporated in the Thesis before the Oral examination.

Based on the scholars research work, his/~~her~~ presentation and also the clarifications and answers by the scholar to the questions, the board recommends that Mr.Tamilarasan.K be awarded Ph.D. degree in the **Faculty of Civil Engineering**.

(Dr. P. Sivashanmugam) 12/4/2019
Indian Examiner

S. T. Ramesh 12/4/19
Subject Expert
(Dr. S. T. RAMESH)

J. Rajesh 12/4/19
Supervisor
(J. RAJESH BANU)

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CERTIFICATE

The research work embodied in the present Thesis entitled **"ENERGETICALLY EFFICIENT COMBINATIVE PRETREATMENT OF MARINE MACROALGAL BIOMASS FOR BIOMETHANE PRODUCTION: EXPERIMENTAL STUDIES, KINETICS AND BIODEGRADABILITY MODELLING"** has been carried out in the Department of Civil Engineering, Anna University Regional Campus, Tirunelveli. The work reported herein is original and does not form part of any other thesis or dissertation on the basis of which a degree or award was conferred on an earlier occasion or to any other scholar.

I understand the University's policy on plagiarism and declare that the thesis and publications are my own work, except where specifically acknowledged and has not been copied from other sources or been previously submitted for award or assessment.

TAMILARASAN K
RESEARCH SCHOLAR

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ABSTRACT

Marine macroalgal biomass is considered a "3rd generation biomass substrates" for biomethane generation, are meeting great awareness due to its mass productivity and more CO_2 diminution effects when compared to 1st and 2nd generation biomass feedstocks. It becomes suitable feedstocks for anaerobic digestion because it contains higher amount of proteins, carbohydrates, lipids and no lignin content. However, to improve the application of anaerobic digestion involving macroalgal biomass, present investigation prefers that there is still some requirement for developing macroalgal biomass digestion potential.

Anaerobic digestion involves the bacterial deterioration of soluble organic matters, sufficient pretreatment improving liquefaction of macroalgal biomass can enhance the anaerobic biodegradability. Several pretreatment techniques such as physical, mechanical, chemical and biological can be overcome the anaerobic digestion drawback. Disperser pretreatment is one of the best potential process for the liquefaction of macroalgal biomass. Still, this pretreatment technique has some limitations such as high energy required and treatment cost. Possibly it can be profitable through disperser mediated chemical liquefaction of macroalgal biomass which leads to improve the methane production rate with the least energy input.

The current research gives the results attained from laboratory scale investigation of disperser mediated chemical agents such as sodium tripolyphosphate, thermo alkali, ozone liquefaction, evaluation of fermentation and methanogenesis activity of liquefied macroalgal biomass. Marine macroalgae (*Chaetomorpha antennina*) samples were collected from

Manapad beach, on the southern coastal region of Tuticorin, Tamilnadu, India (8°22′39″N, 78°3′8″E).

The first study, 12,000 rpm and 30 min of disperser pretreatment conditions was employed to potentially liquefy the macroalgal biomass. In disperser mediated sodium tripolyphosphate, the Sodium tripolyphosphate concentration of about 0.04 g/g TS was considered as an optimum. The outcomes of disperser mediated sodium tripolyphosphate showed higher liquefaction of about 15% than disperser pretreatment (11.7%). The results of biochemical methane potential assay report that disperser mediated sodium tripolyphosphate sample showed higher biomethane production potential of about 0.14 g COD/g COD than the disperser pretreatment (0.11 g COD/g COD). A net gain of 1351 ₹/Ton of macroalgal biomass was achieved in disperser mediated sodium tripolyphosphate than disperser pretreated sample (-10,948 ₹/Ton of macroalgal biomass), respectively.

In the second study, optimized disperser pretreatment conditions were obtained from first study was combined with thermal process. In thermal process, 80^{o}C temperature was employed as effective liquefaction. After that both disperser and thermal conditions were combined with alkali and pH 11 was considered as an optimum for disperser mediated thermo alkali. The outcomes of disperser mediated thermo alkali showed higher liquefaction of about 20% than disperser pretreatment (11.7%). The results of biochemical methane potential assay report that disperser mediated thermo alkaline sample showed higher biomethane production potential of about 0.20 g COD/g COD than the disperser pretreatment (0.11 g COD/g COD). A net gain of 5976 ₹/Ton of macroalgal biomass was achieved in disperser mediated thermo alkali than disperser pretreated sample (-10,948 ₹/Ton of macroalgal biomass), respectively.

A third study, optimized disperser pretreatment conditions were obtained from first study was combined with ozone. In ozone process, 0.00049 g/g TS was considered as an optimum. The outcomes of disperser mediated ozone showed higher liquefaction of about 18% than disperser pretreatment (11.7%). The results of biochemical methane potential assay report that disperser mediated ozone sample showed higher biomethane production potential of about 0.18 g COD/g COD than the disperser pretreatment (0.11 g COD/g COD). A net gain of 2987 ₹/Ton of macroalgal biomass was achieved in disperser mediated ozone than disperser pretreated sample (-10,948 ₹/Ton of macroalgal biomass), respectively.

At last, a comparative study of these three combinative pretreatment achieves maximum liquefaction and biomethane production, based on the economic perspective. Disperser pretreatment followed by thermo alkali gives higher net gain than others.