Preface

In recent years, global water scarcity, rapid urbanization and industrialization have severely stressed available water resources. Along with water scarcity, energy crisis interrelated with environmental degradation and climate change issues have created constant demand for potential biomass, showing sustainable, cost-effective and long-term solutions. Targeting water and energy scarcity together, microalgae-assisted integrated process technologies may provide a potential solution to reduce wastewater pollution and excessive energy load. Towards wastewater treatment and bioenergy production, microalgae as third generation (3G) biofuel are considered of great interest and potential feedstocks due to rapid cell growth, high CO_2 fixation rate, accumulation of lipids and carbohydrate and pollutant removal efficiency from different types of wastewaters. The wastewater medium provides essential nutrients for microalgae growth, and post-treatment water can be used for drinking or irrigation. Proceeding wastewater treatment, cultivated substantial microalgal biomass can be converted into sustainable and green biofuel. Integrating wastewater treatment and biofuel production stimulates the energy transition towards the inevitable bio-economy era via implementing microalgae-based technologies and utilizing biomass streams as biofuel feedstock and renewable sources of input material.

The present thesis demonstrates integrated process development for coal mine water treatment and coal blended biofuel production using a microalgal platform. The main aim is to contribute to sustainable development goals (SDGs) of 6, 7 and 13 related to clean water, affordable clean energy and climate action, respectively. The study is designed in eight different chapters. The first chapter focuses negative impact of coal mine water upon marine ecosystem and soil quality. It discusses different conventional as well as biological strategies to treat coal mine water coupled with energy generation. The second chapter discusses microalgae mediated coal mine water treatment, specifically, biodesalination and heavy metal removal. Further, it elaborates biofuel production from harvested microalgae biomass such as transesterification process for biodiesel production. Then, this chapter insights residual de-oiled microalgae blending with coal via mechanical conversion to form solid briquettes and thermochemical conversion or pyrolysis to form bio-oil and syngas.

The third chapter aims to systematically screen and select candidate microalgae amongst fresh and marine microalgae samples based on coal mine effluent (CME) bioremediation and lipid production. Further, fuel characteristics and thermal analyses were conducted to determine the biofuel properties of different microalgae strains. To perform bioremediation of CME with simultaneous production of microalgal biomass and lipid, water was sampled from the coal main section at Singrauli coalfield (latitude 24.177729°N and longitude 82.65884°E), Madhya Pradesh, India. Different freshwater microalgae strains, *Chlorella pyrenoidosa* (NCIM 2738), *Chlorella protothecoides* (NCIM 5527), *Chlorella minutissima* (procured from Indian Agricultural Research Institute, India) and marine microalgae strains, *Dunaliella sp.* (BDU 10113) and *Chlorella vulgaris* (BDUG D003) were utilized for CME treatment. Amongst these strains, *C. pyrenoidosa* (NCIM 2738) cultivated in CME outperformed with maximum 86.9 % electric conductivity (EC) removal efficiency, 89.8 % chemical oxygen demand (COD) removal efficiency and 2.5 g L^{-1} microalgae biomass concentration. Following lipid extraction of cultivated microalgae, a systematic investigation of thermal behavior and kinetic analysis was conducted for de-oiled microalgae as a biofuel feedstock. The activation energy (E_a) of de-oiled microalgae biomass was calculated using model-fitted Coats Redfern (CR) and model-free distributed activation energy model (DAEM). According to DAEM approach, apparent E_a of *C. pyrenoidosa, C. minutissima, C. protothecoides, C. vulgaris, and Dunaliella* sp. is 55.87 ± 11.16, 56.09 ± 6.32, 46.58 ± 5.55, 55.26 ± 13.14, and 68.09 ± 10.62 kJ/mol, respectively, which is similar to CR approach. The thermodynamic parameters such as enthalpy change (ΔH), Gibbs free energy change (ΔG), and entropy change (ΔS) of studied microalgae are estimated in the range of 41.23–62.74 kJ/mol, 177.87–197.73 kJ/mol, and 0.19–0.22 J/mol•K, respectively. Finally, a one-dimensional convolutional neural network (Conv1D) and long short-term memory (LSTM)-based Conv1D-LSTM model was established to validate thermogravimetry data.

In the fourth chapter, semi-continuous cultivation of candidate microalgae *C. pyrenoidosa* is investigated in bubble column reactor (BCR) and open raceway pond (ORP) targeting nutrient supplemented coal mine effluent (NSCME) treatment. In between different hydraulic retention times (HRTs) of 4 d, 6 d and 9 d, HRT 6 d provided maximum average biomass productivity of 950 mg L^{-1} d^{-1} in BCR and 728.4 mg L^{-1} d^{-1} in ORP. HRT 9 d facilitated a maximum lipid content of 1.8 g L^{-1} in BCR and 1.4 g L^{-1} in ORP. The dynamics of nutrient removal showed HRT 9 d had the maximum COD removal efficiency (96.5% in BCR and 94.2% in ORP) and maximum salinity removal efficiency (93% in BCR and 92% in ORP). Fatty acid methyl esters (FAME) characterization highlighted potential biodiesel applicability with cetane number (CN) of 53.94, saponification value (SV) of 193.33 and Iodine value (IV) of 91.52. The energy dispersive X-ray spectroscopy (EDS) revealed an excess amount of salt and metal ions deposition on the surface of harvested microalgae samples, suggesting bioaccumulation and biosorption as desalination mechanisms. In the next stage, outdoor large-scale *C. pyrenoidosa* cultivation is planned at coal mine sites for 30–35 yr lifespan targeting sustainable water treatment.

The transesterification of lipids in the reactor scale results a substantial amount of de-oiled microalgae accumulation. Aiming circular biorefinery concept, the next three chapters demonstrated the co-processing of this de-oiled microalgae residue with low-rank coal fines as a potential fuel feedstock. Mechanical and thermochemical conversion routes were followed toward sustainable energy development via solid, liquid and gaseous biofuel production.

The fifth chapter aims mechanical conversion to densify de-oiled *C. pyrenoidosa* powder with low-rank coal fines to formulate upgraded biomass-blended coal composites. Fuel characteristics of biomass-blended coal composites of 20:80 ratio showed gross calorific value (19.0 MJ/kg), fuel ratio (1.85), and low sulfur content (< 1%). The multi-objective optimization strategy is used to optimize the molding pressure, average particle size, and binder ratio to maximize the mechanical performance indicators such as compressive strength and drop strength of biomass-blended coal composites. The blended composites showed a maximum compressive strength of 14.6 MPa and a drop strength of 97.8% at multi-objective optimized conditions after model validation (R^2 > 0.99).

Thermogravimetric, derivative thermogravimetric and differential thermal analyses (TGA-DTG-DTA) were conducted to determine characteristic temperature points and heat involvement during combustion. TGA-DTG-DTA showed remarkable shifting of ignition point from 335 °C (parent coal) to 301–299 °C (blended coal composites), extended burnout temperature (47–82 °C higher than parent coal) and excessive exothermic heat involvement (3305–3363 µVs/mg) during composite combustion. Further, Levenberg-Marquardt (LM) algorithm–based artificial neural network (ANN) model was applied to validate the thermal analysis of coal, microalgae and blended composites, which offers an excellent tool for studying thermochemical conversions.

In sixth chapter, a co-pyrolysis-based valorization of de-oiled microalgae and low-rank coal blend was performed to generate syngas emission. Targeting hydrogen and methane as a global energy carrier and promising fuel, a novel approach is applied to maximize hydrogen and methane cumulatively in terms of the hymethane carrying ratio defined as (H_2 + CH_4)/ (CO + CO_2) by applying optimization strategies. Pyrolysis kinetic models, Kissinger- Akahira-Sunose (KAS) and Starink (STK), are used to evaluate apparent E_a. The gradual addition of microalgae (0–100%) in coal reduces E_a from 189.11–55.87 kJ/mol and 180.16–54.61 kJ/mol by KAS and STK method, respectively. The maximum hymethane carrying ratio is observed 2.51 and 3.51 at optimized conditions of response surface methodology (RSM) and ANN based multi-objective genetic algorithm (ANN-MOGA), respectively. Maximum H_2 (54.5 %) in the syngas is observed at the mid pyrolysis stage (451 °C) using ANN-MOGA optimized conditions (blending ratio– 42.25 % and heating rate–13.8 °C/min). Considering the specific advantage of ANN-MOGA over RSM, the application of MOGA with ANN as a multi-task machine learning algorithm is recommended to modernize the co-pyrolysis process for hymethane rich syngas emission.

In the seventh chapter, a cleaner co-pyrolysis strategy was established for high-quality bio-oil production for low rank coal (CL), de-oiled microalgae (ALG), and their blends (CLALG). The heavy metal-loaded Cu-Cr-ZSM-5 catalyst is synthesized by using ion-exchange method and investigated in the CL, ALG and CLALG pyrolysis bio-oil upgradation at different catalyst feed ratios (0.5:1, 1:1, 2:1). The synthesized catalyst was characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Brunauer-Emmett-Teller (BET) analysis. The synthesized catalyst is nano-crystalline with an average size of 7 nm. The microstructure of the synthesized catalyst shows stacked nanorods packing with connected intercrystal and intracrystal mesopores. The catalytic and non-catalytic pyrolysis of CL, ALG and CLALG were performed at 600 °C, 10 °C/min for 60 min. The non-catalytic ALG pyrolysis has shown maximum bio-oil yield (35.7%). The synergistic effect of nanorod morphology, active acid sites and excess mesoporosity of catalyst facilitates efficient deoxygenation, denitrogenation and aromatization of pyrolysis bio-oil with oxygen content from 2.1–3.1%, nitrogen content 3.5–5.1% and aromatic content 49.4–54.4% at a catalyst feed ratio of 1:1. The maximum obtained high heating value (HHV) of bio-oil from catalytic pyrolysis of CL (40.1 MJ/kg) followed by CLALG (38.6 MJ/kg) and ALG (36.5 MJ/kg) is very close to diesel oil with HHV (42–46

MJ/kg). Further, a co-pyrolysis mechanism is proposed to investigate possible catalytic action sites to yield high-quality bio-oil. These outcomes enrich information regarding catalyst development, catalyst feed interaction and thermocatalytic cracking as emerging efforts towards industrial-scale upgradation of bio-oil to engine fuels. The eighth chapter provides conclusion and future perspective of present work.

Thus, the present thesis successfully meets a coupled function of mine water treatment and biofuel production following a closed-loop process using a microalgae platform. Contributing to sustainable energy solutions and different SDGs, accumulated de-oiled microalgal biomass was efficiently co-processed with coal fines for solid, liquid and gaseous fuel production to gain carbon neutral energy and zero waste discharge.