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Catalytic gasification of algal biomass for hydrogen-rich gas production: Parametric optimization via central composite design

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ABSTRACT

This study presents the optimization of algal biomass catalytic gasification for hydrogen-rich gas production. Three operating parameters under varying conditions of temperature (700–900 °C), catalyst loading (5–20 wt%) and reaction time (15–40 min) were optimized. The central composite design (CCD) was used to perform optimization and to investigate the influence of operating parameters on response variables (fractions of H_2, CO, CO_2 and CH_4). The results indicated the temperature and catalyst loading as the most significant reaction parameters influencing H_2 production and reducing the tar produced during the gasification process. The highest H_2 fraction of 48.95 mol% (18.77 mol kg-biomass^{-1}) was obtained at an optimum condition at 851 °C with catalyst loading of 16.4 wt% and reaction time of 28.8 min. The high R^2 values of 0.98, 0.97, 0.95, and 0.90 corresponding to the response variables (H_2, CO, CO_2 and CH_4) showed paramount estimation of model.

1. Introduction

Fossil fuels have been the primary source of world's energy supply by contributing more than 80% of global energy demand [1]. However, the dwindling fossil fuel assets and the associated climate change (i.e. greenhouse gas emissions, CO_2) are the key challenges of the world energy and environment. This scenario has induced researchers to seek for alternative and renewable sources of cleaner and environmental friendly energy production for sustainable development. Among all the clean energy carriers, hydrogen is an appealing choice due to its high calorific value (122 MJ kg^{-1}), where its combustion gives off highest quantity of energy per gram and only release pure water as final product. The industrial scale hydrogen production has been predominantly either based on natural gas and coal via steam reforming and gasification systems [2]. However, recent development in producing hydrogen from edible crops (i.e. sugar cane, wheat, grains and sugar beet, etc.) and non-food plant biomass [3–5], is a promising alternatives to fossil fuels which have limited reserves, cause excessive global climate change, and requires high capital cost to exploit. Nevertheless, biofuel production from aforementioned biomasses have major agronomical influences on high value products mainly food production, arable land requirement, technological impediments for their conversion to useful products and cost-effectiveness; these make hydrogen production economically less appealing [6,7]. Moreover, lignocellulosic biomasses are causing key downstream conflicts in the removal or conversion of remaining lignin to support and maximize the hydrogen gas conversion and production competences [8]. Algae derived biofuels are getting considerable attention globally due to the following reasons: low concentration or absence of highly complex components such as hemicellulose and lignocellulosic, fast growth rate, non-edibility and substantial amounts of simple carbohydrates, proteins and lipids [9,10]. The application of microalgae as a biofuel source can likely overcome numerous of the identified problems associated to terrestrial crops cultivation, i.e. land use and conflict with food use. Moreover, microalgae can also be grown in the vicinity of the process sites such as power plants, wastewater treatments and other industrials sources to harvest the maximum amount of anthropogenic CO_2 (biosequestration) into desired metabolites. This in turn will contribute to the tremendous reduction of GHG emssions. Thermochemical conversion technologies include pyrolysis, torrefaction, liquefaction, gasification and direct combustion to convert algal biomass to biofuels. Among the technologies, gasification is considered to be the most efficient process dealing

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with algal biomass conversion.

Gasification converts variety of feedstocks into hydrogen (H_2), carbon monoxide (CO), and methane (CH_4) with a wide range of hydrocarbon chain. Concerning the gasifying agent, air, oxygen and steam and/or a mixture of these are frequently used gasifying agents. The yield of a desired gas product highly depends on the feedstock as well as operating conditions including temperature, reaction time and catalysts [11]. The syngas (H_2 + CO) product can be used for feeding efficient gas engines, gas turbines, power in Integrated Gasification Combined Cycle (IGCC) systems and synthesis of other value-added chemicals such as methanol and dimethyl ether (DME) e.g., via Fischer-Tropsch process [12–15]. However, the tar formation, char and carbon deposition are practically unavoidable during gasification. Thus, tar cracking, unreformed volatile fragments, and carbon deposition, etc. have become the major obstacles in algal biomass gasification. Similarly, the catalyst free gasification produces higher CO content owing to the low propensity of water-gas shift (WGS) reaction ($CO + H_2O \leftrightarrows H_2 + CO_2$) to the right and elevated reaction temperatures are deriving force of H_2 production and high biomass conversion [7,16]. Whereas, the application of a catalyst is an advantage to circumvent the demand of extreme reaction conditions, accelerate reaction rates, increase hydrogen yield and eradicate the tar as well as char occurrence [10]. Likewise, the presence of nickel-based (Ni) catalyst accelerates the splitting of C—C bond, minimalize C—O bond (which supports methanation reaction) and preferably, favor the WGS reaction [17,18], thus exhibiting high reactivity in tar cracking and light-hydrocarbon reforming.

Recently, many researchers have explored the potential of various catalysts for decomposing tar produced during algal biomass gasification [10,19]. Additionally, they enhance WGS reaction which produces hydrogen. Díaz- Díaz-Rey et al. [20] investigated Ni-based catalysts (Ni, Ni–Pt and Ni–Rh) to gasify *Scenedesmus almeriensis* algal biomass. Among them, Ni–Pt was found the most effective catalyst for tar reforming and promoting WGS and Boudourad reactions to favor hydrogen content in gaseous fraction. Similarly, Onwudili et al. [10] demonstrated the positive effect of NaOH and Ni—Al_2O_3 for gasifying three different microalgae species (*Saccharina latissima*, *Spirulina platensis* and *Chlorella vulgaris*) via supercritical water approach. Hydrogen yields were over two times higher in the presence of NaOH than in its absence and tar yields were reduced up to 71%. *Saccharina latissima* gave the highest hydrogen gas yield of 15.1 mol kg^{-1}. Duman et al. [19] reported the effects of an iron catalyst (Fe_2O_3—CeO_3) on steam gasification of *Nannochloropsis oculata* alga biomass. And they found crucial role of catalyst for reducing tar formation in the range of 53–70%, besides enhancing WGS reaction. Moreover, Norouzi et al. [21] investigated Fe-Ni/γ-Al_2O_3 catalyst for supercritical water gasification of *Enteromorpha intestinalis*. Maximum hydrogen production was found to be 12.28 mmol g^{-1} of *E. intestinalis*. Recently, algal hydrochar (solid residue of algae gasification) has been used as a catalyst for gasification [22,23].

However, higher content of CO_2 and tar resulting from the aforementioned studies on algal biomass gasification are still a key challenge.

Knowing that CO_2 is produced together with H_2 during WGS reaction and thus capturing CO_2 could be helpful to shift the WGS reaction towards H_2 and thus converting more CO and H_2O into H_2. Calcium oxide (CaO) due to its high sorption capacity and cost-effectiveness, has been widely accepted as a CO_2 sorbent [24–26] and also employed in sorption enhanced steam reforming to improve the H_2 production [27]. Besides, CaO has also been reported as an active tar cracking catalysts [28,29]. However, due to high gasification temperatures, sintering and coke deposition limits the CaO thermostability for CO_2 sorption. Recently, ZnO has been found an excellent secondary dopant, which prevents CaO sintering and improve the performance of the NiO—CaO [25]. Moreover, ZnO tends to promote WGS reaction [25,30,31]. Both Ni and CaO catalysts application in algal biomass gasification has been reported in literature to some extent. However, on the basis of our knowledge, active tri-metal oxide catalyst such as modified CaO with addition primary (Ni) and secondary (ZnO) dopants and air as a gasifying agent has never been considered for algal biomass gasification reaction.

Central composite design is a useful scientific approach which has been successfully applied for optimizing gasification operating parameters and other related multifactor problems [7,32,33]. This approach entails the design of experiments and multiple regression analysis to evaluate the influence of multiple process variables on response variables. Suitability of the intended model can be divulged by means of the diagnostic verifying tests stipulated by analysis of variance (ANOVA) [32]. Its principal benefit is generating necessary information and establishing the optimum conditions for desired responses with a reduced number of experiments.

In this work, catalytic air gasification performance of *Chlorella vulgaris* microalgae biomass in the presence of tri-metal oxide catalyst for hydrogen-rich gas production has been investigated using central composite design approach. The key novel investigations of this study were:

- To evaluate the multifactor (combined) parametric effects (temperature, catalyst loading and reaction time) on response variables during the gasification process.
- To determine the optimum conditions, within the experimental parameters range to maximize the desired response variable.

2. Materials and methods

2.1. Biomass feedstock

Microalgae biomass (*C. vulgaris*) powder (~100 mm particle size) was provided by Pure Bulk Inc (USA) and processed for catalytic gasification. Table 1 shows the characteristics of biomass. Method corresponding to each analysis are described in our previous research [7,34].

2.2. Catalyst

Table 2 shows the characteristics of catalyst utilized for algal biomass gasification. ZnO—Ni—CaO catalyst was prepared via wet impregnation method using CaO as a base catalyst and added with the primary ($Ni(NO_3)_2$ $6H_2O$) and secondary dopant $Zn(NO_3)_2$. Deionized water was used to dilute 5 wt% of Ni and 5 wt% of ZnO (secondary

Table 1
Feedstock characterization.

Feedstock	Proximate analysis				Ultimate analysis (wt.% Dry basis)					HHV (MJ kg^{-1})	Molar formula C1 basis
	M[a]	VM[b]	FC[c]	Ash	C	H	N	S	O*		
C. vulgaris	6.3 ± 0.3	83.5 ± 0.1	3.8 ± 0.4	5.1 ± 0.3	50.39 ± 1.6	6.01 ± 0.7	14.77 ± 3.3	6.05 ± 0.5	22.78 ± 2.0	22.19	$C_1H_{1.418}O_{0.339}N_{0.251}S_{0.045}$

[a] Moisture.
[b] Volatile matter.
[c] Fixed carbon.
* By difference: (100% − (H + N + S + C)).