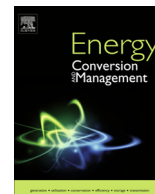




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# Hydrothermal gasification performance of *Enteromorpha intestinalis* as an algal biomass for hydrogen-rich gas production using Ru promoted Fe–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocatalysts

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## ABSTRACT

Supercritical water gasification (SCWG) of *Enteromorpha intestinalis* (*E. intestinalis*) as a major algal biomass of southern coast of Caspian Sea was investigated in a batch reactor with and without the catalyst, to determine its potential for hydrogen production. The highest hydrogen yield of 5.25 (mmol H<sub>2</sub>/g of *E. intestinalis*) was observed for the noncatalytic test in the temperature of 440 °C, water loading of 6 g, *E. intestinalis* loading of 0.06 g and reaction time of 10 min. All catalytic tests were performed in this condition in the presence of unpromoted and ruthenium promoted Ni–Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocatalysts. Catalysts were prepared with 12 wt.% of Ni and 6 wt.% of Fe in the active phase and 0.5–2 wt.% of Ru as a promoter via microemulsion technique. Nanocatalysts were characterized by ICP, BET, XRD, H<sub>2</sub> chemisorption, and TEM techniques to recognize their physicochemical properties. According to catalyst characterizations, the promoted Ni–Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 2 wt.% Ru with higher dispersion and smaller size of nickel on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, showed the best performance during SCWG of *E. intestinalis*. The maximum H<sub>2</sub> yield of 12.28 (mmol H<sub>2</sub>/g of *E. intestinalis*) and hydrogen selectivity of 0.74, were obtained by using this optimized catalyst.

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## 1. Introduction

Needless to say, world's population is being increased fast. Food and energy security are the concerning challenges human faced in the 21st century. Sustainability in generation, consumption and conservation of energy should be the top priorities for approaching a sustainable energy development [1]. Global warming and the widespread use of fossil fuels, such as petroleum, coal and natural gas, cause several environmental impacts which inspired many researchers to find alternative energy resources and more efficient technologies. Hydrogen has been regarded by many scientists as the key energy carrier of the future with much higher energy density than other conventional fuels [2,3]. However, hydrogen is not produced in natural processes and can't be found in its pure form in nature [4]. Most of the hydrogen worldwide is produced from steam reforming of methane. However, the use of algal biomass as a suitable alternative to fossil fuels has gained extensive attention for the production of green hydrogen in recent years

[5]. Algal biomass is an abundant and renewable resource which is rich in carbon and hydrogen [6]. Agricultural wastes as lignocellulosic materials have been utilized by different conversion technologies for producing second generation biofuels besides other applications such as animal feed or polymer industries [7]. Recently, research and development in bioenergy have been focused on utilization of the third generation of biofuels (biofuels derived from algal biomass) [8]. Over 28 million tons of marine biomass promises a renewable and environment friendly resource for the production of biofuels and chemicals [9]. This kind of biomass has no competition with agricultural food and feed production [10]. The low content of hemicelluloses and about zero content of lignin in the structure of algal biomass results in easier and faster hydrolysis which results in better hydrothermal conversion [11]. Two major routes are defined for biomass-based hydrogen production [12–14].

- Biochemical conversions including biological photosynthesis, biological water–gas shift (WGS) and biological fermentation.
- Thermochemical conversions including pyrolysis, partial oxidation and SCWG.

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Conventional thermochemical processes face major problems such as the formation of tar and chars [15,16]. Condensed tar on downstream equipment may polymerize to a more complex structure, which is undesirable for hydrogen production [17,18]. Furthermore, wet biomass can be a major challenge for conventional gasification and makes its process energy intensive and not economically viable. Gasification in supercritical water media can efficiently overcome these shortcomings, especially for wet biomass [19–21]. Various environmental pollutants of industrial or agricultural origin results in the severe eutrophication of coastal areas which itself is the main reason for the excessive blooming of macroalgae [22]. As the macro algae dies and drifts into the water, the coastal area faces ecological and socioeconomic problems. Some parts of the Caspian Sea coast are in danger of excessive blooming of macro algae. Thus, there is a big social demand to determine an industrial utilization for the blooming filamentous *E. intestinalis* algae [23,24]. It seems necessary to explore an efficient and cost effective process for conversion of this bio-resource. Electricity can also be generated from high-pressure gas obtained from gasification of algae for industrial use in the presence of large scale cultivation units [25]. Marine macroalgae do not need fresh water or fertilizers to grow and shorter life cycles make them more favorable for cultivation than their terrestrial counterparts. So, an efficient continuous system in the presence of cultivation units will make the process economically viable and commercial [26]. Some work have been done on gasification of algal biomass for hydrogen production. Deniz et al. investigated the hydrothermal gasification of *Posidonia Oceanica* in a batch reactor without using the catalyst. The maximum H<sub>2</sub> yield of 10.37 mol/kg at 600 °C was observed [27]. Raheem et al. investigated the optimum condition for hydrogen production via gasification of *Chlorella vulgaris* in a horizontal tubular furnace. Maximum hydrogen molar fraction of 42% was obtained at the temperature of 703 °C [28].

It is known from the literature that nickel based catalyst has been used in the SCWG of biomass [29,30]. Also, it is well understood that catalysts with smaller active metal particle size and high rate of dispersion promises more efficient catalytic activity [31]. Li et al. reported that the intensity of diffraction peaks of NiO decreased with the addition of Cu species in Ni–Cu. It was also observed that Cu can mitigate the sintering of alumina [32]. However, some reports have shown that the peak area of H<sub>2</sub> consumption increased with increasing of Fe additive amount for Ni–Fe/Al<sub>2</sub>O<sub>3</sub> catalysts with Fe/Ni ≤ 0.5 [33]. On the other hand, Fe has a co-catalytic function. Since Fe has high oxygen affinity than Ni, the addition of Fe to Ni catalysts can improve the steam reforming reaction [34].

In this study, *E. intestinalis* as an algal biomass has been used for hydrogen-rich gas production via gasification in supercritical water media. Fe–Ni supported on γ-Al<sub>2</sub>O<sub>3</sub> has been used as the catalyst. Experiments first performed without adding the catalyst to determine the optimum conditions for maximum hydrogen yield. Then, unpromoted and Ru promoted catalysts are added to observe the effect of the catalyst on the yields of different products and hydrogen yield. The main novel investigations of the current study are mentioned below

- Utilization of *E. intestinalis* as major macroalgae of southern coastal area of Caspian sea for production of hydrogen via hydrothermal gasification for the first time.
- Using Fe–Ni alloy instead of Ni as a metal catalyst for better cracking of longer chain hydrocarbons and higher conversion into the gas phase.
- Holistic analysis of products of a third generation biomass feedstock for further use in the industrial sector as an alternative energy resource in the future.

## 2. Materials and methods

### 2.1. Feed materials

The selected macroalgae used in the present study was *E. intestinalis*. The *E. intestinalis* was collected from Sisangan area located in Southern Caspian Sea, Iran, where a stable coverage was found. They were dried under atmospheric conditions for 48 h and ground to a particle size < 150 μm in diameter. The elemental analyzes of the biomasses were performed using CHNS analyzer (Vario ELIII by Elementar, Germany). The weight percentage of oxygen was determined through Eq. (1). Also, the components in the structure of biomass were analyzed by the method of Goering and Van Soest [35].

$$O\% = 100 - C\% - H\% - N\% - S\% - Ash\% \quad (1)$$

### 2.2. Catalysts preparation

The catalysts were prepared using reverse microemulsion techniques with a mass fraction of 12% Ni, 6% Fe and mass fractions of 0.5%, 1%, 1.5% and 2% Ru on γ-Al<sub>2</sub>O<sub>3</sub> as support. Table 1 presents the prepared catalysts.

Prior to catalyst preparation, γ-Al<sub>2</sub>O<sub>3</sub> was treated with air calcination at 400 °C for 4 h to remove its pores water content and probable combustible impurities. Furthermore, Ni–Fe–Ru nanoparticles were synthesized through reverse microemulsion using Triton X-100 as a nonionic surfactant, n-hexane as the oil phase, and n-butanol as co-surfactant. The weight percentage of metals (Ni, Fe and Ru) loading were carefully adjusted with preparing appropriate aqueous solutions of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Ru(NO)(NO<sub>3</sub>)<sub>3</sub>. Catalysts were synthesized with water to surfactant molar ratio of 0.16. After obtaining microemulsion mixture on vigorous stirring, hydrazine hydrate was added in excess to improve nanoparticle formation in cores of the micelles through metal oxides reduction. The certain amount of γ-Al<sub>2</sub>O<sub>3</sub> was added to the mixture. Next, tetrahydrofuran (THF) was added to the mixture as an emulsion destabilizing agent with the rate of 0.1 ml/min during a 2 h period. The mixture was left in a static situation to settle, and then decanted. The sediment was recovered using vacuum filtration over ashless filtration paper and washed several times with distilled water and ethanol [36]. The catalysts were dried at 120 °C for 2 h and calcined under an air flow at 400 °C for 4 h for removing the traces of surfactant and ammonia.

### 2.3. Catalyst characterization

The metal loadings of the calcined catalysts were verified by an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) system. Temperature Programmed Reduction (TPR) with H<sub>2</sub> was performed in the fixed bed flow reactor. The TPR profiles of samples were recorded from room temperature to 1123 K for 50 mg of catalysts under 30 ml/min flow of H<sub>2</sub> and Ar mixture, with H<sub>2</sub>/Ar molar ratio of %5. The heating rate was 10 K/min and the temperature was maintained at 1123 K for 30 min after it

**Table 1**  
The prepared catalysts.

Catalyst name	Catalyst formula
C1	12%Ni–6%Fe on γ-Al <sub>2</sub> O <sub>3</sub>
C2	0.5% Ru–12%Ni–6%Fe on γ-Al <sub>2</sub> O <sub>3</sub>
C3	1%Ru–12%Ni–6%Fe on γ-Al <sub>2</sub> O <sub>3</sub>
C4	1.5%Ru–12%Ni–6%Fe on γ-Al <sub>2</sub> O <sub>3</sub>
C5	2%Ru–12%Ni–6%Fe on γ-Al <sub>2</sub> O <sub>3</sub>

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