# A review of the catalytic gasification of different algae in supercritical water (SCW)

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**Abstract.** Among various biomass, algae have unique advantages such as fast growing, high efficient photosynthesis, no competition with crops etc. Supercritical Water Gasification (SCWG) is a potential technology for converting algae biomass into gases (including $H_2$, $CH_4$, CO, $CO_2$), with merits with higher gas yield and lower tar and char etc. A review of the catalytic gasification of different algae in Supercritical Water (SCW) is presented here, summarizing the past research about the gas yield and distribution in production and their corresponding conditions and valuable conclusions for various algae. Finally, based on the literatures above-mentioned, future directions in this field are suggested.

## Introduction

A brief introduction of algae biomass energy. With the development of world economy, more and more fuel is desired. However, traditional fossil fuels are non-renewable resource, pollute the environment and produce green gases during combustion process. Thus, it is necessary to seek an environmentally-friendly and renewable substitution for fossil fuels. Biomass is an ideal, renewable energy. Obtaining energy from biomass could help to relieve fossil energy crisis and would not increase $CO_2$ content in air. Algae have properties of short cultivation cycle, high photosynthetic efficiency, high gas yield, which are considered as a promising substitution for addressing the energy crisis and environmental issues associated with fossil fuel use [1].

Supercritical water gasification (SCWG) reaction. For converting high-moisture biomass such as algae, conventional gasification technologies has low thermal efficiency due to the desire of water vaporized in feedstock, which results from the fact that conventional biomass gasification processes require a dry feedstock. The energy required exceeds the energy that is needed to dry the feedstock prior to gasification. Hence, the energy utilized to remove water from wet biomass feedstock is lost as water evaporates. Supercritical water gasification (SCWG) is considered as the most promising method. SCWG is defined as an reaction process by physical-chemical change under the condition of $Tc \geq 647$ K and $Pc \geq 22.1$ MPa. In supercritical water, water is miscible with small organic compounds and gases [2], so a homogeneous phase reaction could exist at SCWG conditions after the solid biomass particles decompose and dissolve. In addition, SCWG process results in high gas yield and low yields of tar and char [3]. More importantly, the process of SCWG is with no need for drying feedstock, which reduces energy consuming during operating process. Due to advantages above-mentioned, SCWG technology for converting algae into gases like $H_2$, $CH_4$, CO, $CO_2$ has potential development prospects.

The research on SCWG of algae started from Antal in 1990. With more and more desire of renewable energy, more researchers have focused on it. Although there are not many research about it, they performed experiments about SCWG of different algae and obtained several valuable results.

## SCWG of different algae species

At present, the research on SCWG of algae primarily focused on *Spirulina*, *Chlorella*, *Nannochloropsis* and others such as *Saccharina latissima*, *Phaeodactylum tricornutum*, *Scendesmus quadricauda*.

*Spirulina*. *Spirulina* is a kind of common algae with high proteins and carbohydrates [4], which is often considered as healthy food boosting the body's defenses. In addition, it has also potential application in SCWG. Onwudili et al [5] provided a comparison of SCWG (500 °C, 30 min reaction time, 36 MPa, 15 wt% feedstock concentration) among *Spirulina platensis*, *Chlorella vulgaris* and *Saccharina latissima* in the presence/absence of NaOH and/or $Ni/Al_2O_3$ and obtained that the gas yield of feedstock was 69 % without NaOH and $Ni/Al_2O_3$. When NaOH was used, water-soluble products were the predominant reaction products and the gas yield was 23 % and 20 % with only NaOH and NaOH and $Ni/Al_2O_3$, respectively. Moreover, composition of gases yielded was different with or without NaOH and/or $Ni/Al_2O_3$. NaOH could help to increase $H_2$ yield and reduce $CO_2$ yield substantially, which rose the calorific values of gases. Miller et al [6] studied SCWG of *Spirulina* in the absence of catalysts under the condition of 550-600 °C, 4-9 s residence time, 25 wt% feedstock concentration and 23.5 MPa and analyzed factorial experiments results. Notably, the reactor utilized was a plug flow reactor, different from common batch reactor. Thus, the residence time was very short (only several seconds) compared with usual reaction time (often several minutes). The results indicated that temperature and residence time had significant effects on gasification efficiency (GE) and gasification rate. A maximum gasification rate was obtained when $\tau \leq 2$ s, which could be due to the onset of turbulent flow as indicated by a high Reynolds number.

*Chlorella*. *Chlorella* is a green unicellular alga with low-lipid high-protein content, found in both fresh and marine waters usually [7] and it is also as food-grade material. Onwudili et al [5] researched SCWG of *Chlorella vulgaris* under the condition of 500 °C, 30 min reaction time, 36 MPa and 15 wt% feedstock concentration in the presence/absence of NaOH and/or $Ni/Al_2O_3$ and he found that the gas yield was 67 % without NaOH and $Ni/Al_2O_3$, which indicated that gas products were the dominant reaction products when no catalysts or only the nickel-catalyst was used. However, water-soluble products were the predominant reaction products and the gas yield was 24 % with only NaOH used and NaOH and $Ni/Al_2O_3$ used. Meawhile, composition of gases yielded was various with or without NaOH and/or $Ni/Al_2O_3$. For *Chlorella*, $H_2$ yield increased from 18.3 mol% to 57.3 mol% accompanied without $CO_2$ yielded when only NaOH was used. Chakinala et al [8] investigated SCWG of *Chlorella Vulgaris* at varying operating conditions such as temperature (400-700 °C), reaction time (1-15 min), feedstock concentration (2.9 wt%, 7.3 wt%) and the addition of catalysts ($Ru/TiO_2$, $NiMo/Al_2O_3$, $P_tP_d/Al_2O_3$, $CoMo/Al_2O_3$, inconel powder, Ni wire). He observed that the dry gas composition of uncatalyzed gasification of *Chlorella Vulgaris* in SCWG mainly contained $CO_2$, CO, $CH_4$, $H_2$, and some $C_2$-$C_3$ compounds. The higher gasification efficiency (GE) needs higher temperatures, lower algae concentrations, and longer residence times and the highest GE was 84 % at 600 °C and 2 min reaction time with nickel-based catalysts. Complete gasification required higher temperatures (700 °C) and excess amounts of ($Ru/TiO_2$) catalyst. He also demonstrated that adding catalysts could help to obtain higher yields of $H_2$ and lower CO yields via enhanced water-gas shift activity. Minowa and Sawayama [9] performed experiments of *Chlorella Vulgaris* at low temperature (350 °C) in the presence of nickel catalyst and proposed a new method of cultivation of algae in the recovered solution obtained from the low-temperature (near critical) catalytic gasification of algae and they obtained a methane-rich gas with carbon conversion ranging between 35 and 70 %. Moreover, they also found all nitrogen in the microalga was converted to ammonia. Raheem et al [10] optimized SCWG of *Chlorella vulgaris* under varying conditions of temperature (500–900 °C), microalgal (*Chlorella vulgaris*) biomass loading (0.6–2.5 g), heating rate (5–25 °C/min), and equivalent ratio (ER = 0.1–0.35) via central composite design (CCD). He also achieved a number of valuable results and he presented that temperature was the most significant process parameter influencing $H_2$ production, followed by biomass loading and heating rate. The optimum $H_2$ yield was

41.75 mol% under the condition of 703 °C, biomass loading of 1.45 g, a heating rate of 22 °C/min, and an ER of 0.29.

*Nannochloropsis*. *Nannochloropsis sp.* is a marine algae with high-lipid content [11]. There are several studies about it. Guan et al [12] reported a systematic study of the gasification of *Nannochloropsis sp.* in supercritical water at 450–550 °C. He found that the main gas production contained $H_2$, $CO_2$ and $CH_4$ and lesser amounts of CO, $C_2H_4$ and $C_2H_6$. Similarly with research about *Chlorella*, more rigorous reaction condition (including higher temperatures, longer reaction times, higher water densities, and lower algae loadings) favored higher gas yields. The feedstock concentration strongly affected the $H_2$ yield, which more than tripled when the concentration decreased from 15 wt% to 1 wt%. In addition, the water density had little effect on the gas composition. Guan et al [13] investigated the effect of catalyst Ru/C on SCWG of *Nannochloropsis sp.* at 410 °C and the gasification efficiency was only 45 % at 75 min, 4.3 wt% feedstock concentration and a catalyst loading of 1 g/g (mass of Ru/C catalyst/mass of dry algal biomass). He proposed catalyst loading had the most significant effect on both the yields and composition of the gaseous products. When the catalyst loading reached 2 g/g, complete gasification of the microalga was achieved. Brown et al [14] converted *Nannochloropsis sp.* into gas production via SCW from 200 to 500 °C with 60 min in the absence of any catalyst and obtained the highest $H_2$ yield was 39 % at 400 °C, 5 wt% feedstock concentration. He also found that the major combustible gases were $H_2$ and $CH_4$, with smaller amounts of $C_2H_4$ and $C_2H_6$, similar with the research of Guan et al [15]. Furthermore, very little or no CO was presented during the temperature range, and it could be due to water-gas shift and/or methanation reactions strengthened.

Others. There are few research about other algae. Onwudili et al [5] considered *Saccharina latissima* as the feedstock of SCWG and found that the gasification efficiency was 65 % without any NaOH and $Ni/Al_2O_3$. Significantly, the gasification efficiency decreased to 12 % and 14 % with only NaOH used and NaOH and $Ni/Al_2O_3$, respectively. However, $H_2$ mole yield increased from 25 % to 69 % with the addition of NaOH and $Ni/Al_2O_3$, accompanied with lower $CO_2$ mole yield. Haiduc et al [16] investigated the influence of nickel on the growth of *Phaeodactylum tricornutum*, a trace contaminant that might accumulate upon effluent recycling. He proposed the existence of nickel adversely affected the growth of algae, and if the nickel concentration was 25 ppm, the cell division of algae could be inhibited completely. The gas production of SCWG of *Phaeodactylum tricornutum* with Ru/C was methane-rich gas with gasification efficiency (68–74 %) and $C_1$–$C_3$ hydrocarbon yields of 0.2 $g_{C1–C3}/g_{DM}$ (DM, dry matter). Tiong et al [17] studied SCWG of *Scenedesmus quadricauda* (low protein and high carbohydrate contents) at 385 °C, 15 min, 26 MPa and 5 wt% feedstock concentration with or without nickel catalyst. He proposed that the yield could reach 80–90 % with the catalyst but the one was only 12 % in the absence of catalyst. For non-catalytic SCWG, the predominant gas product was carbon dioxide, which may be resulted from decarboxylation of algae. For catalytic SCWG, the major gaseous products were $CH_4$, $CO_2$, $H_2$, CO and its order of concentration was $CH_4 > CO_2 > H_2 >$ CO.

## Conclusion and future directions

For algae feedstock, supercritical water gasification (SCWG) is a very potential technology for producing gases. As far as we're aware, it can offer efficient conversion from algae to gases, avoid water phase-changing heat dissipation and improve the recycling process of nutrients and metal elements, in favor of follow-up use of them.

Algae are composed of proteins, polysaccharides and lipids primarily. Different algae differ from percentage compositions of these three substances. Although some investigators have proposed proteins could be hard to gasification, it could be conquered via selecting appropriate reaction condition and catalysts. Therefore, different algae species may result in different optimal reaction parameters, gases yields, carbon gasification efficiencies and distributions of products. However, the research about SCWG of algae was few and this summary of SCWG of different algae can provide a research overview for further investigation in the very potential field with rapid development.

In the future, the research about the cell structure change of algae in SCW need to be studied more deeply. Various algae produce different compositions of solid and aqueous products, which may be necessary to quantify in follow-up separation processing for reasonably development and utilization. Moreover, the reaction kinetic research for feedstock and some intermediate products need to be devoted to the field to explore the reaction mechanism of SCWG completely.

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