Thermodynamic assessment of gasification and pyrolysis of marine algae to produce hydrogen-containing gas

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Abstract. The article gives a thermodynamic assessment of modes of gasification and pyrolysis of algae of gross formulation $C_1H_{1.66}O_{1.4}$ with obtaining hydrogen gas. The authors investigate the modes of air gasification and pyrolysis of algae at pressures of 0.1 MPa and 1 MPa with varying the fuel excess ratio and temperatures. In the case of gasification at a pressure of 0.1 MPa the hydrogen and carbon monoxide concentration increases with an increase of the fuel excess ratio (φ) from 2 to 10 and at $\varphi = 10$ and $T = 1000$ K reaches 25.95 mole % and 27.84 mole %, respectively. An increase in temperature from 1000 K to 1300 K leads to a decrease in the amount of hydrogen and an increase in carbon monoxide in the gaseous products. An increase in the operating pressure from 0.1 to 1 MPa at a gasification temperature of 1000 K leads to the formation of a small amount of methane (~ up to 5 mole %), a decrease in the mole content of hydrogen and carbon monoxide in the final products, and also to the formation of coke (at $\varphi \geq 7$), which we can use as a target product. The caloric value of the gases produced is higher in the pyrolysis of algae than in its gasification. The pressure increase at 1300 K has almost no effect on the equilibrium composition of the products in the gaseous products.

1 Introduction

Algae has gained recognition as an alternative source of biomass for energy production because of its wide distribution, high growth rate, and simple growth conditions [1]. Algae is a carbon-neutral fuel because of its photosynthesis, absorbing carbon dioxide from the atmosphere [2]. Using algae as a fuel also has disadvantages: low volume weight, high handling, transportation, and storage costs [3], so people burn dry algae directly for heat and/or electricity close to where they grow [4]. Scientists today more often consider the gasification of algae to produce synthesis gas, a versatile raw material for both power generation and chemical synthesis [5].

Gasification is an autothermal process of converting the organic part of solid fuel into a combustible gas in the absence of an oxidizer [6]. Several processes occur simultaneously during gasification, spatially separated by the length of the gasifier: drying (100-200°C),

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pyrolysis (200-600°C), combustion (600-1200°C), and cooling. The drying stage removes moisture, then the fuel is pyrolyzed in an oxygen-free environment with the formation of a coke residue, which is oxidized in the combustion zone, and then the ash residue is cooled before being discharged from the reactor [7]. Combustible gas is formed during gasification and comprises hydrogen, carbon monoxide, carbon dioxide, methane, and water vapor.

The efficiency of gasification depends on many parameters, such as the type and humidity of fuel, flow rate and type of oxidizer, type of gasifier (fixed bed, fluidized bed, etc.), temperature, pressure, and fuel excess ratio [8, 9]. Temperature is the most influential factor in the thermochemical methods of hydrogen production since these reactions are endothermic. High process temperature ensures the completeness of carbon conversion and reduces the number of resins [10]. The pressure in the gasifier reactor is an important control parameter that affects the composition of the gaseous products. Increasing the operating pressure usually increases the caloric content of the resulting combustible gas [11]. At higher operating pressure, operational difficulties of such equipment arise [12]. An important characteristic of the hydrogen-containing gas is the H_2/CO ratio to determine the optimal operating conditions of the gas generator [13]. The major obstacle to the use of algae as a raw material in their large-scale gasification is excessive moisture [14, 15].

We can apply various methods of numerical simulation of system behavior to estimate the performance of heat-generating plants, and the quality of the resulting gaseous fuel, and also to calculate the overall efficiency of the process under study [16, 17]. The kinetics of any thermochemical fuel oxidation process can play a key role in determining the number of final products.

This work assesses the gasification and pyrolysis of algae thermodynamically to produce hydrogen-containing gas.

2 Methodology

We can perform thermodynamic calculations of the equilibrium composition of reaction products to study multicomponent systems by finding the minimum Gibbs free energy or finding the system state with maximum entropy [18].

We performed thermodynamic calculations of the equilibrium composition of algae gasification/pyrolysis products using the TERRA program to find the conditions for obtaining gaseous products with the highest hydrogen concentration [19]. We calculated a system comprising algae (gross formula $C_1H_{1.66}O_{1.4}$ taken from [20]), nitrogen, and oxygen (air), varying the process temperature (1000-1300 K) and the fuel excess ratio (φ). We varied the values of φ between 2 and 10 (lack of oxidizer), and if the fuel excess ratio is unity, the fuel is completely oxidized to carbon dioxide and water. We performed a separate calculation for the case of pyrolysis of a model algae composition - without adding an oxidizer to the system. The pressure in the calculations is 0.1 MPa (atmospheric) and 1 MPa. The results showed an equilibrium composition of gasification/pyrolysis products at a temperature, pressure, and fuel excess ratio. The minimum temperature value was 1000 K, since the chemical reaction rates decrease at lower temperatures and the equilibrium values of reaction product concentrations will take a long time to reach [21].

3 Results and discussion

Gasification of algae at atmospheric pressure.

Figure 1 shows the dependences of the molar content of algae gasification products on the fuel excess ratio φ at a temperature of 1000 K.

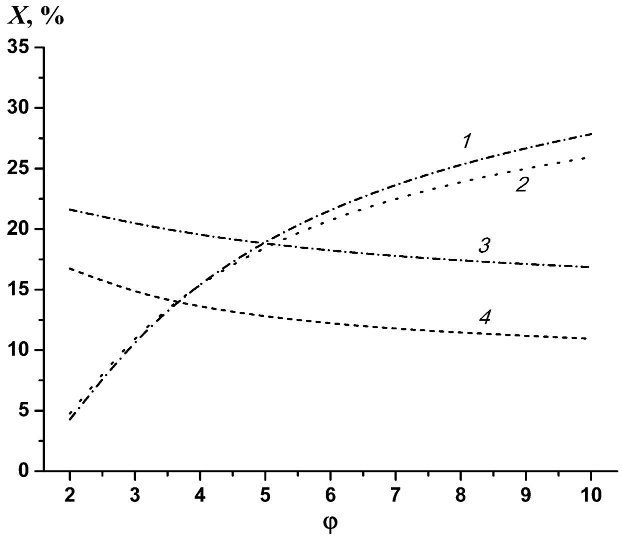

Fig. 1. Dependences of the molar product content (X) on the fuel excess ratio φ during gasification of marine biomass $C_1H_{1.66}O_{1.4}$ at 1000 K at a pressure of 0.1 MPa. Curves 1 - CO, 2 - H_2, 3 - CO_2, 4 – H_2O.

An increase in the fuel excess ratio from 2 to 10 leads to an increase in the hydrogen concentration from 4.76 to 25.95 mol %. The concentration of carbon monoxide also increases with increasing φ and reaches the value of 27.84 mol % at φ = 10. The content of water vapor and carbon dioxide slightly decreases with increasing φ over the entire range under study. The H_2/CO ratio increases from 0.93 to 1.11 as the excess fuel ratio decreases from 10 to 2.

Figure 2 shows the dependences of the mole content of the algae gasification products on the fuel excess ratio at 1300 K.

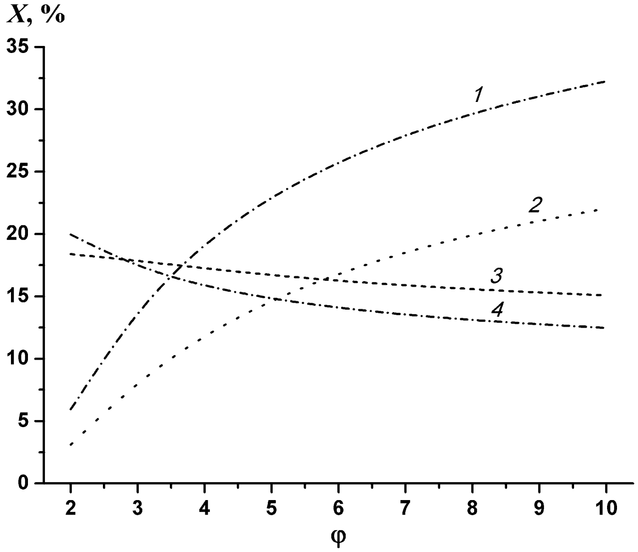

Fig. 2. Dependences of molar product content (X) on the fuel excess ratio in gasification of marine biomass $C_1H_{1.66}O_{1.4}$ at 1300 K and at 0.1 MPa. Curves 1 - CO, 2 - H_2, 3 - CO_2, 4 – H_2O.

When φ increases from 2 to 10, the hydrogen content increases from 3.1 to 22.04 mol %. The concentration of carbon monoxide has a similar dependence and reaches the value 32.25 mol % at φ = 10. The content of water vapor and carbon dioxide decreases with increasing φ, as in the previous case. The pattern of change in the H_2/CO ratio is opposite to the previous case: it increases from 0.52 to 0.68 with an increase in the fuel excess ratio from 2 to 10.

An increase in temperature by 300 K (from 1000 K to 1300 K) leads to a slight decrease in hydrogen and an increase in carbon monoxide in the gaseous products. This is because of a shift in the chemical equilibrium of the exothermic reaction of water gas to the left: $CO + H_2O = CO_2 + H_2$. We must keep in mind that the H_2/CO ratio at 1300 K is lower than at 1000 K, which may prevent the use of the resulting hydrogen-bearing gas in obtaining various hydrocarbons in the Fischer-Tropsch processes.

Gasification of algae under increased pressure.

Figure 3 shows the mole content dependences of algae gasification products on the fuel excess ratio φ at a temperature of 1000 K and increased pressure (1 MPa).

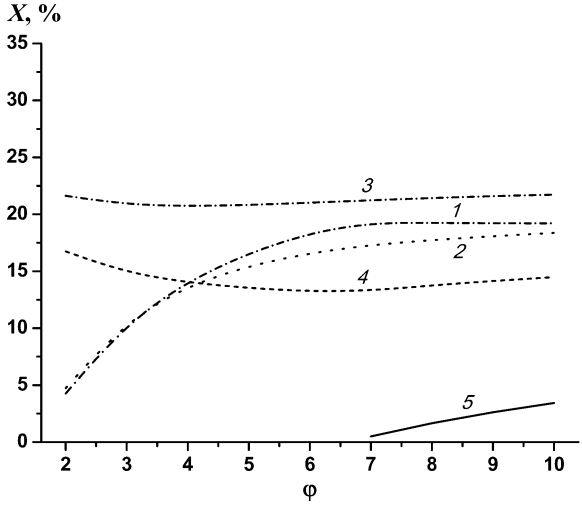

Fig. 3. Dependences of molar product content (X) on the fuel excess ratio in gasification of marine biomass $C_1H_{1.66}O_{1.4}$ at 1000 K and at 1 MPa. Curves 1 - CO, 2 - H_2, 3 - CO_2, 4 – H_2O, 5 - C (solid).

We observe an increase in the hydrogen concentration from 4.73 to 18.37 mol % with increasing φ, within the limits considered. The content of carbon monoxide increases from 4.26 to 19.27 mol % when the excess fuel ratio increases from 2 to 7, and then falls slightly (at φ>7). The molar content of carbon dioxide changes insignificantly and is about 20-22 mol %. The water vapor content decreases as φ increases from 2 to 6 and then increases slightly (at φ>7). The H_2/CO ratio increases from 0.96 to 1.11 with a decrease in the fuel excess ratio from 10 to 2, similar to the case of gasification at atmospheric pressure at the same temperature (1000 K).

Increasing the pressure according to the Le Chatelier's principle shifts the chemical equilibria toward reducing the volume of the resulting gaseous products. This should lead to an increase in the concentration of carbon dioxide and condensed carbon by the Boudoir reaction: $2\ CO = CO_2 + C$ (solid). The decrease in the concentration of carbon dioxide does not occur when the concentration of carbon monoxide increases in our case, just because of the Boudouard reaction taking place. At φ=7 condensed carbon appears in the system and its content increases to 3.43 mol % at φ=10. The methane content increases from 0.01 to 3.37 mol % with an increase in the fuel excess ratio from 2 to 10. Methane formation occurs because of the reaction of hydrogasification: $C(solid) + 2H_2 = CH_4$, and the reaction of methanation: $CO + 3H_2 = CH_4 + H_2O$. Figure 3 does not show the mole content of methane because of the close values with the mole content of condensed carbon.

The calculation of the dependence of the molar content of algae gasification products on the fuel excess ratio at a temperature of 1300 K and a pressure of 1 MPa showed that increasing the pressure at this temperature has almost no effect on the equilibrium composition of gaseous products. This shows that the effect of temperature is more important for the establishment of equilibrium than the effect of pressure.

We performed additional similar calculations on algae gasification at increased pressure to find the gasification temperature at which no coke formation occurs. We saw no coke formation when the temperature was increased from 1000 to 1100 K, and the resulting gas at $\varphi=10$ has the following composition of the major products (mol %): H_2 – 23.01, CO – 28.69, CH_4 – 0.01, CO_2 – 15.94, H_2O – 12.98.

Pyrolysis of algae.

When the fuel excess ratio tends to infinity, we realize the case of pyrolysis, i.e., the calculation system has no additional oxidizer, but uses oxygen from the algae composition. Table 1 contains the results of the equilibrium composition of the algae pyrolysis reaction products. Regularities similar to the case of gasification as a function of temperature characterize algae pyrolysis. The difference consists in the composition of the gaseous products: the mole content of the target products becomes higher (hydrogen, carbon monoxide, and methane), and the caloric value of the gas increases. We condense the distinctive feature of this thermochemical process in the pyrolysis products carbon at a temperature of 1000 K and a pressure of 1 MPa. The coke yield is ~4.23 g per 100 g of algae (gross formula $C_1H_{1.66}O_{1.4}$). However, pyrolysis requires external energy input. The table does not include the composition of pyrolysis products at 1300 K and 1 MPa pressure, as they are almost identical to those got at 1300 K and 0.1 MPa pressure. The table includes a calculation of the equilibrium composition of pyrolysis products at 1100 K and pressure of 1 MPa, which shows the absence of coke formation (as with gasification under similar conditions).

Table 1. Concentrations of the major pyrolysis products of algaealgae depend on the conditions of their production.

[H_2O], mol %	**[H_2], mol %**	**[CO], mol %**	**[CO_2], mol %**	**[$C_{(c)}$], mol %**	**[CH_4], mol %**	**T, K**	**p, MPa**
8.76	35.71	40.47	14.25	0	0.01	1000	0.1
12.33	33.02	45.12	9.53	0	0	1300	0.1
18.43	21.4	18.96	23.43	12.72	5.06	1000	1
11.5	30.38	40.01	14.93	0	0.03	1100	1

We can conventionally consider the modes of gasification and pyrolysis of algae with coke production as processes with a negative carbon balance if we consider that algae is a carbon-neutral fuel, in which CO_2 is captured from the total carbon cycle (in cases of carbon extraction and use or coke residue burial).

So in the present work, we excluded cases with the addition of water vapor to reduce the process temperature and increase the hydrogen content (and the H_2/CO ratio).

4 Conclusion

We performed thermodynamic calculations of chemical equilibria of algae gasification/pyrolysis products with the gross formula $C_1H_{1.66}O_{1.4}$ to determine the conditions for obtaining gas with the highest hydrogen content. We can use them to estimate the composition of hydrogen-containing gas produced by algae gasification/pyrolysis. Increasing the fuel surplus ratio leads to higher carbon monoxide and hydrogen content in algae gasification and pyrolysis. An increase in the operating pressure from 0.1 to 1 MPa at a gasification temperature of 1000 K results in the formation of a small amount of methane (~ up to 5 mol %), a decrease in the mole content of hydrogen and carbon monoxide in the final products, and also in coke formation (at $\varphi \geq 7$). Increasing the temperature from 1000 K to 1300 K reduces the amount of hydrogen and increases the amount of carbon monoxide in the gasification products. Increasing the pressure at 1300 K has almost no effect on the equilibrium composition of the products in the resulting hydrogen-bearing gas.

The optimal operating pressure from the point of view of using gaseous products obtained during algae gasification/pyrolysis is 0.1 MPa and the temperature is 1000 K.

Regularities of hydrogen-containing gas composition change, similar to the gasification process, characterize algae pyrolysis. The difference occurs at the temperature of 1000 K and pressure of 1 MPa: condensed carbon appears in the pyrolysis products. The coke yield is ~4.23 g per 100 g of algae with the gross formula $C_1H_{1.66}O_{1.4}$.

We can vary the composition of the gasification/pyrolysis products depending on the needs of the consumer by control parameters: pressure, temperature, and fuel excess ratio. You can use the resulting hydrogen-containing gas to generate heat and/or electric power and, in cases of condensed carbon formation, as a fertilizer or adsorbent.

We performed the study within the framework of the State Assignment. The state registration number is №AAAA-A19-119022690098-3 and №122012500156-1.

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