Two-step separation of bio-oil from condensed products of hydrothermal liquefaction of microalgae

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Abstract. Present paper is devoted to the study of the process of bio-oil separation from condensed products of hydrothermal liquefaction (HTL) of microalgae (MA). In this work we proposed a two-step separation. Proposed separation method produces separately "light" (with density less than 1 g/cm³) and "heavy" (with density more than 1 g/cm³) fractions of bio-oil. "Light" bio-oil is separated mechanically from the aqueous solution. "Heavy" bio-oil is produced by solvent (dichloromethane) extraction and subsequent solvent evaporation. The solvent in the proposed method doesn’t contact with aqueous solution. The last makes the utilization of aqueous solution safer. The total yield of "light" and "heavy" bio-oil is 34.7 % (at 330 °C and 1 hour). It is almost the same as the yield of bio-oil obtained by the “standard” solvent separation method (35.1 %). The elemental composition of "light" bio-oil differs from the "standard" bio-oil by a lower content of carbon, and a greater content of hydrogen and oxygen. "Light" bio-oil contains more easily boiled compounds than "standard" bio-oil. In particular, the content of the fraction with boiling point less than 200 °C in "light" bio-oil is 7 % higher than in "standard" bio-oil (28 vs. 21 %).

1. Introduction

Microalgae (MA) are one of the most promising sources of renewable biofuels. An important problem for MA to biofuel processing is high humidity of MA. To convert wet biomass to biofuel, so-called hydrothermal technologies can be used ("hydrothermal" means a process carried out in the presence of water or steam at a temperature above 100 °C; recently, we have had experience in hydrothermal technologies in a variety of applications [1–7]).

In the case of MA, the technology of hydrothermal liquefaction (HTL) has been of great interest in recent time. The main product of HTL is bio-oil [6–7]. One of the main advantages of HTL is the unnecessary of a preliminary drying stage for the raw biomass. MA can be supplied to the HTL reactor in the wet state, in which they come after harvesting from the cultivator. An additional advantage is that in the HTL process, not only lipids contribute to the yield of bio-oil (as in the process of biodiesel production), but also carbohydrates and proteins, that increases the total yield of the product [8].

HTL products are bio-oil, aqueous solution, solid residue and gaseous products [6]. An aqueous solution containing a significant amount of dissolved organic substances is proposed to be used as an additive to the medium for MA cultivation. The chemicals that are contained in the aqueous solution can serve as a source of nutrients for MA growth. Researches in this direction are actively being carried out at the present time [9–11].
Various organic solvents such as dichloromethane [12–13], chloroform [14], acetone [15], exane [16] are usually used to separate the bio-oil from the aqueous solution and the solid residue. The solvent is usually added to the mixture of bio-oil, aqueous solution and solid residue. Then the solvent is separated from the mixture and evaporated. The resulting product is considered as a bio-oil. As a rule, the organic solvents used are limitedly soluble in water. Work with such aqueous solution is difficult. Before further use or disposal of such aqueous solution, it is required to remove the remaining organic solvent.

In this paper, a two-step process for bio-oil separation from condensed products of MA HTL has been studied. After the HTL process and reactor cooling, the aqueous solution with a part of the bio-oil and solid residue are withdrawn into a separate container, in which the "light" bio-oil, whose density is less than the density of the aqueous solution, is separated by gravity separation. HTL product that is remained within the reactor (it consists from solid residue and bio-oil concentrated mainly on the internal walls of the reactor) is treated with a solvent. The product obtained after evaporation of the solvent (whose density is usually slightly higher than the density of water) is referred to as "heavy" bio-oil. The yield of bio-oil and its chemical and fractional composition are studied in this work. A comparison with standard method of solvent separation is also carried out.

2. Experimental
In HTL experiments the *Spirulina* was used. *Spirulina* was produced by the Lomonosov Moscow State University, the Faculty of Geography, the Laboratory of renewable energy sources. Algae were pre-dried at 100 °C in a Binder VD53 drying oven (Germany).

Two stainless steel reactors with a volume of 30 cm³ were used. Each reactor was loaded with 3 grams of dried algae and 12 grams of distilled water. Then, both reactors were closed with a lid (sealed) and placed in a sand bath. The sand bath was heated to 330 °C at a rate of about 7 °C/min. The residence time at 330 °C was 60 minutes. Inside the reactors, a pressure close to the pressure of saturated water vapor corresponding to a temperature of 330 °C was established. Then, the heater was turned off and the reactors cooled down to room temperature. Then the reactors were opened. From the first reactor, the easy-flowing products (a mixture of an aqueous solution with a part of solid residue and bio-oil) were removed and placed in a plastic tube. Dichloromethane (20 g) was added to the remaining HTL products (mainly, the remaining solid residue and bio-oil) in the first reactor, and the reactor was closed. In the second reactor, the HTL condensed products were not removed, and dichloromethane (20 g) was added to the reactor, and the reactor was closed. The solvent extraction in the closed reactors lasted two days with a periodic rotation of the reactors to ensure a more complete contact of the solvent with the internal surface of the reactors. After that, the contents of the two reactors were placed in separate plastic tubes.

Thus, three plastic tubes were obtained: 1 – a mixture of an aqueous solution, a solid residue and a so-called "light" bio-oil produced in the first reactor; 2 – dichloromethane solution with a mixture of undissolved solid residue and a so-called "heavy" bio-oil obtained in the first reactor; 3 – two unmixed liquids with different densities and colors (from above – aqueous solution, from below – dichloromethane solution with so-called "standard" bio-oil) and undissolved solid residue obtained in the second reactor. The "light" bio-oil was separated from the aqueous solution with a spoon. Bio-oil ("heavy" and "standard") from the dichloromethane solution was obtained by evaporation at 35 °C. A sample of dichloromethane solution was taken from the volume of the solvent using a syringe and placed in Petri dishes. The exposure in the evaporation oven was stopped after the mass of the Petri dish had stabilized and remained unchanged for 2 hours. The mass was measured using an analytical balance Sartorius Cubis MSA324S.

Elemental analysis (content of C, H, N, O, S elements) of the samples was carried out using the Thermo Scientific Flash 2000 HT analyzer (the oxygen content was calculated by subtraction). Each sample was examined at least five times, after which the mean value and error (not exceeding 5 %) were determined.
The fractional composition of bio-oil was studied by a thermogravimetric analysis (TGA) using a thermal analyzer STA PT1600 (Linseis GmbH). A sample of bio-oil in an amount of about 50 mg was placed into a corundum crucible. Heating of the crucible was carried out in argon atmosphere. The heating rate to 500 °C was 2 °C/min, then the heating rate to 800 °C was 5 °C/min.

3. Results and discussion
The values of the bio-oil yield are presented in table 1. The values of the yield of "light" and "heavy" bio-oil obtained in the two-stage separation were 15.7 % and 19.0 %, respectively. The total output of bio-oil in the two-stage separation thus amounted to 34.7 %. This is by 0.4 % less than the yield of bio-oil obtained by the "standard" solvent separation. This result indicates that the organic compounds dissolved in water, upon contact of the aqueous solution and the dichloromethane solution, are practically not soluble by the organic solvent, but remain in the aqueous solution. Obtained results lead to a conclusion about the effectiveness of two-step separation. Results showed that two-step separation is not inferior to standard separation. At the same time, a two-stage separation makes the utilization (processing) of the aqueous solution safer, because the aqueous solution does not come into contact with the dichloromethane solution and, accordingly, does not saturate with this organic solvent.

Table 2 shows the elemental composition of the bio-oil samples. In the "standard" bio-oil (obtained at 330 °C and by "standard" separation), the carbon content was 73.7 %, the concentrations of hydrogen, oxygen and nitrogen were 6.0, 11.1 and 6.2 %, respectively. The elemental composition of the "light" bio-oil differed from the "standard" by a lower content of carbon and a greater content of hydrogen and oxygen. This could be due to the remnants of water in the "light" bio-oil. The chemical composition of the "heavy" bio-oil was close to the chemical composition of the "standard" bio-oil. In general, the chemical composition of the bio-oil, as defined in this work, is consistent with the chemical composition of the bio-oil samples obtained earlier by hydrothermal treatment of the Spirulina in other works [15, 17].

Figure 1 shows the results of TGA analysis for bio-oil samples. Figure shows TGA curves for the samples of "light" bio-oil obtained by two-step separation, and "standard" bio-oil. It can be seen that the "light" bio-oil contains more easily boiling compounds. The weight of "light" and "standard" bio-oil samples at heating to 800 °C decreased by approximately 82 % and 72 %, respectively. The share of the gasoline fraction (weight change at 200 °C) in the sample of "light" bio-oil was about 28 %. The share of the gasoline fraction in "standard" bio-oil was about 21 %.

### Table 1. The results of the determination of the yield of bio-oil.

| Reactor | Bio-oil reference | Initial raw loaded into the reactor | Bio-oil yield, g | Bio-oil yield, % |
|---------|-------------------|-----------------------------------|-----------------|-----------------|
| I       | "Light"           | 0.47                              | 15.7            |
| I       | "Heavy"           | 0.57                              | 19.0            |
| II      | "Standard"        | 1.05                              | 35.1            |

### Table 2. Elemental composition of bio-oil samples.

| Reactor | Bio-oil reference | Content, wt. % |
|---------|-------------------|----------------|
|         |                   | C   H   O   N   S |
| I       | "Light"           | 65.2 8.5 18.9 6.2 1.2 |
| II      | "Heavy"           | 74.9 6.0 9.1 6.0 2.8 |
| II      | "Standard"        | 73.7 6.0 11.1 6.2 3.0 |
Figure 1. The change in the mass of the samples of bio-oil in the process of heating in an argon atmosphere: 1 – sample of "light" bio-oil, 2 – sample of "standard" bio-oil, 3 – temperature versus time in the TGA experiment.

4. Conclusion
The process of two-stage separation of bio-oil from condensed products of HTL of MA has been studied. By the two-stage separation we obtained separately "light" (with density less than 1 g/cm$^3$) and "heavy" (with density more than 1 g/cm$^3$) fractions of bio-oil. The proposed separation makes it possible to avoid the contact of the organic solvent with the aqueous solution, that makes the utilization of the latter safer. At the same time, the total yield of "light" and "heavy" bio-oil is almost the same as the yield of bio-oil obtained by the "standard" solvent separation method. It has been established that the elemental composition of "light" bio-oil differs from the "standard" bio-oil by a lower content of carbon, and a greater content of hydrogen and oxygen. The results of TGA experiments showed that "light" bio-oil contains more easily boiled compounds than "standard" bio-oil. In particular, the content of the gasoline fraction in "light" bio-oil is 7 % higher than in "standard" bio-oil (28 versus 21 %).

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