Hydrothermal liquefaction-isomerization of biomass for biofuel production

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Abstract. During the last years, a lot of research activity has been devoted to a biomass conversion into liquid fuels. In order to produce fuels of the same quality as those obtained from crude oil, an appropriate conversion technology is required. Hydrothermal liquefaction (HTL) of biomass is a catalytic process that is considered to be a very promising technology for biofuel production. HTL products have a relatively high content of gasoline and diesel fractions, low oxygen content and high heating value. Moreover, HTL does not require a drying of the raw materials prior to conversion that allows a significant reduction of the price of the biofuel. We developed a new catalytic system for HTL, consisting of halloysite nanotubes as aluminosilicate carrier and strontium/titanium/tin oxide as an isomerizing component. Due to the sufficiently high specific surface area of halloysite nanotubes, a higher content of gasoline fraction in biocrude products was achieved. In addition, the introduction of the isomerizing component significantly increased the octane number of the gasoline fraction.

1. Introduction
Currently, many methods have been proposed for the conversion of biomass into liquid hydrocarbons. Two main approaches can be distinguished: 1) processing of individual components of biomass (in particular, hydrolysis of cellulose followed by fermentation to obtain bioethanol, transesterification of triacylglycerides); 2) conversion of biomass as it is. The second approach includes pyrolysis that can be carried out either in the presence of hydrogen (hydropyrolysis) or without it, and hydrothermal liquefaction (HTL) to produce bio-oil. Of all the methods, the HTL process is the most economically feasible, since its implementation does not require energy-intensive deep drying of biomass, as in the case of pyrolysis. At the same time, raw materials with moisture content of 50–90% by weight are quite suitable for processing. Thus, the biomass of green plants, aquatic vegetation or microalgae can be converted directly into bio-oil [1]. During the HTL process, biomass is subjected to rapid heating in a closed volume to a temperature of 250-600 °C, and then it is kept at the maximum temperature for a while. Then the reaction mass is cooled, and fractioned.

The main products of the HTL process are: a mixture of methane and C2-C3-hydrocarbon gases, a mixture of liquid hydrocarbons or bio-oil, aqueous phase containing ammonium nitrogen, carboxylic acids and other water-soluble organic substances, and solid residues. The heating rate, maximum temperature and exposure time can be varied during the process. The most valuable component is bio-oil, so the HTL process is usually carried out under such conditions that maximize its yield. In particular, the use of catalysts increases the yield of bio-oil and usually helps to reduce the process temperature, and in some cases affects the quality of the product as well.
To assess the quality of bio-oil, such indicators as fractional composition (gasoline and diesel fraction content) oxidative stability of individual fractions, and density are used. In addition, the following indicators are of particular interest from practical point of view: the octane number of the gasoline fraction and the low-temperature properties of the diesel fraction.

For example, in patent [2] authors describe a heterogeneous catalyst for hydrothermal liquefaction of biomass consisting of a hydrogenating component (ruthenium) and porous carrier with pore volume of 30-60 %. However, the use of the noble metal as a hydrogenating component greatly increases the total cost of the catalyst and the entire technological process.

Homogeneous catalysts are also used for hydrothermal liquefaction of microalgae biomass [3]. The increase in bio-oil yield for various catalysts occurs in the following order: Na2CO3 > CH3COOH > KOH > HCOOH. However, usage of organic acids as catalysts leads to increased nitrogen content in the bio-oil, compared to the bio-oil obtained with alkali catalysts. One of the disadvantages of using homogeneous catalysts is that they are consumed during the process and cannot be regenerated, which leads to low economic efficiency of the process.

Biller and coauthors [4] studied three heterogeneous catalyst of the following composition: Co/Mo/Al2O3, Pt/Al2O3 and Ni/Al2O3. A 10 % increase in low heating value of the bio-oil and decrease of oxygen content in the products was observed, while there was no significant yield change detected. It was found that Co/Mo/Al2O3 and Pt/Al2O3 catalysts have a greater effect on carbohydrates and proteins of biomass, while Ni/Al2O3 reduces the oxygen content in the products of lipids decomposition.

Saber and coauthors [5] studied effect of various catalysts (nano-Ni/SiO2, zeolite and Na2CO3) on the yield and quality of bio-oil at low temperatures (210 °C, 230 °C, 250 °C) produced from microalgae Nannochloropsis sp. It was established that the use of catalysts leads to a decrease in the content of oxygen and nitrogen in bio-oil while increasing the yield; bio-oil yield decreases in the series: nano-Ni/SiO2 > zeolite > Na2CO3. The maximum yield was achieved with nano-Ni/SiO2 catalyst is achieved at a temperature of 250 °C and was 30%.

The efficiency of using HZSM-5 and Ce/HZSM-5 catalysts was demonstrated by Xu and coauthors on Chlorella pyrenoidosa microalgae [6].

Another heterogeneous catalyst for the HTL process is described in patent [7]. The catalyst consists of nickel oxide on the surface of powdered clay. The surface area of the catalyst is relatively low (10-15 m2/g) which hinders transport of biomass components towards catalyst’s active centres, that leads to increased content of high-boiling components in the product. In addition, the absence of isomerization activity of the used catalyst leads to a low quality of the product (octane number of the gasoline fraction of the bio-oil does not exceed 66).

Table 1 shows summarized literature data on the processes of hydrothermal liquefaction of microalgae biomass.

| Microalgae strain  | T, °C | Exposure time, min | Catalyst          | Yield, % | Source |
|-------------------|------|-------------------|-------------------|----------|--------|
| Cyanobacteria sp. | 325  | 45-60             | -                 | 21.0     | [8]    |
| Bacillariophyta sp.| 325  | 45-60             | -                 | 18.2     | [8]    |
| Chlorella pyrenoidosa | 280  | 120               | -                 | 39.4     | [9]    |
| Aurantiochytrium sp. K RS101 | 400  | 10                | -                 | 51.2     | [10]   |
| Nannochloropsis sp. | 600  | 1                 | -                 | 67.0     | [11]   |
| Nannochloropsis sp. | 250  | 60                | nano-Ni/SiO2      | 30.0     | [5]    |
| C. pyrenoidosa     | 300  | 20                | HZSM-5           | 34.0     | [6]    |
| C. pyrenoidosa     | 300  | 20                | Ce/HZSM-5        | 49.9     | [6]    |
| Spirulina / Chlorella | 350  | 60                | 1 M Na2CO3       | 20.0/27.3| [12]   |
| Spirulina / Chlorella | 350  | 60                | 1 M KOH          | 15.2/22.4| [12]   |
| Spirulina / Chlorella | 350  | 60                | 1 M HCOOH        | 14.2/19.1| [12]   |
As can be seen from Table 1 in modern works, the yield of bio-oil reaches 50-60% wt. of the original microalgae biomass. A large fraction of carbon is transformed in water-soluble form. The yield of gaseous products is about 20%. The dominant component in gaseous products is CO$_2$. In addition, gaseous products may contain small amounts of N$_2$, CH$_4$, and C$_2$-hydrocarbons.

The use of catalysts, both homogeneous and heterogeneous, is considered one of the promising ways to improve the method of HTL which is currently not well developed [14]. An alternative to catalytic HTL may be the catalytic upgrading of bio-oil in a separate process, following hydrothermal liquefaction [15].

The goal of this work is to develop a new catalyst in order to increase the efficiency of hydrothermal liquefaction of biomass. We used Al$_2$O$_3$, kaolin and halloysite as carrier for the catalyst. Halloysite is a natural aluminosilicate clay consisting of nanosized tubes. Its unique structure and low cost make it of particular interest for using as a catalyst component. Halloysite TEM micrograph is shown in Figure 1.

In this paper, we investigated not only the yield of hydrothermal liquefaction products, but also the properties of the resulting gasoline and diesel fraction. In particular, an attempt was made to increase the catalyst isomerizing activity by adding oxides of strontium, titanium and zirconium. In our opinion, this should have contributed to an increase in the content of branched hydrocarbons in the products, which in turn should contribute to the increase of octane number of the gasoline fraction and improvement of the low-temperature properties of the diesel fraction.

![Figure 1. TEM micrograph of halloysite nanotubes.](image-url)
2. Methods

The catalyst was prepared as follows. 18 g of finely dispersed halloysite clay nanotubes or Al₂O₃ or kaolin and 1 g of isomerization agent (tin oxide, titanium oxide, zirconium oxide) were grinded and mixed. 150 g of 10 % solution of polyvinyl alcohol with molar mass of 6000 (pore-forming component) and 1.5 g of 85 % solution of orthophosphoric acid (binder component) were added to the mixture. Then the mixture was pushed through an extrusion device, dried for 5 h at 140 °C and then tempered at 400 °C for 10 h. Then the mixture was soaked in 50 g of 10 % solution of sulfuric acid for 1 h followed by drying at 250 °C for 5 h.

The catalyst’s activity was evaluated using 150 g of cyanobacterium Anabaena variabilis biomass. The biomass and 5 g of the catalyst were placed in an autoclave, heated up to 300 °C at a rate of 70 °C/min under vigorous stirring and kept at this temperature for 30 minutes. Then the autoclave was cooled to the room temperature and the products were separated into liquid and solid phases by filtration followed by liquid phase separation into aqueous and organic phases in a separating funnel. The weight of organic phase was measured and bio-oil yield was calculated.

To estimate bio-oil fraction composition it was dehydrated and distilled. The following fractions were collected: initial boiling point – 180 °C (gasoline fraction) and 180 °C – 360 °C (diesel fraction). The hydrocarbon composition of the gasoline fraction was analyzed using a gas chromatograph, and the octane number of the fraction is calculated from the analysis results. To assess the low-temperature properties of the diesel fraction, its pour point is measured.

3. Results

The yield of bio-oil was 37 % of the dry weight of the biomass taken. Fraction analysis of the bio-oil showed that the content of gasoline fraction was 54 % wt., and 39 % wt. for diesel fraction. The residues accounted for the rest.

The octane number of the gasoline fraction, calculated from the results of chromatographic analysis, was 86. The pour point of the diesel fraction was minus 7 °C.

The results of experiments with various catalysts are shown in Table 2.

| Isomerization agent | Finely dispersed component | Organic phase yield, % | Gasoline fraction content, % | Research octane number | Diesel fraction content, % | Pour point of the diesel fraction |
|---------------------|---------------------------|------------------------|----------------------------|------------------------|---------------------------|----------------------------------|
| SnO                 | Al₂O₃                     | 37                     | 54                         | 86                     | 39                        | - 7                              |
| TiO                 | kaolin                    | 36                     | 55                         | 88                     | 38                        | - 10                             |
| ZrO                 | halloysite                | 34                     | 45                         | 86                     | 52                        | - 10                             |
| SnO                 | clay                      | 26                     | 15                         | 60                     | 41                        | 0                                |
| TiO                 | nanotubes                 | 21                     | 14                         | 54                     | 65                        | 2                                |
| ZrO                 |                           | 20                     | 32                         | 73                     | 64                        | - 6                              |

As can be seen from the presented results, the use of all three isomerizing agents in combination with finely dispersed aluminum oxide leads to an increased yield of liquid products of hydrothermal liquefaction, as well as increase in the content of high-octane hydrocarbons in the gasoline fraction, and, in addition, a significant decrease in the pour point of the diesel fraction. It should be noted that the diesel fraction with a pour point in the range from -5 to -10 °C is quite suitable for the production of winter-grade diesel fuel. The average octane number of the gasoline fraction in the resulting products is 87 points, which is also a good result that exceeds a gasoline fraction obtained without a catalyst by 10-20 points [7, 16, 17].
When using kaolin and halloysite as a fine and porous component the yield of liquid products does not increase. Moreover, the content of high-boiling components in the bio-oil significantly decreases. This fact suggests that, Al₂O₃, also exhibits significant cracking activity.

The increased yield of bio-oil can be explained by the activity of the catalyst due to its greater specific surface area, and the presence of isomerization component. At the same time, a high value of the specific surface of the catalyst leads to an increased content of the gasoline component, while the isomerizing component is responsible for increase in the octane number of the gasoline fraction. Moreover, the described catalyst also improves low-temperature properties of the diesel component of the bio-oil due to the increased content of branched hydrocarbons in the latter.

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