
THERMAL AND CATALYTIC DECOMPOSITION STUDIES OF MICROALGAL RESIDUE USING PYROLYSIS-GC/MS AND TG/MS

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Abstract

The marine algal biomass is one of the most promising candidates for the raw material of sustainable biofuel production. Biofuels of different phases can be converted by bio- or thermochemical methods. In this study thermogravimetry/mass spectrometry (TG/MS) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) were used to analyze the main decomposition products of the deoiled algal cake (DAC). Two mesoporous silica catalysts (SBA-15 and FSM-16) were applied to modify the composition of the evolving gas phase products. The yield of the evolving volatile gas products was enhanced by the use of the SBA-15. This catalyst promoted the decomposition of the inorganic carbonates into carbon dioxide. The formation of hydrocarbons during the fast pyrolysis simple alcohol molecules were formed from the deoiled algal residue. The yields of the anhydro-sugar derivatives were strongly affected by the presence of both catalysts. The intensity of the aromatic and aliphatic decomposition products were influenced by the catalytic decomposition procedure.

Keywords: algae, mesoporous silica catalysts, pyrolysis, thermogravimetry, mass spectrometry

1. Introduction

The algae can be utilized in several ways to produce biofuels [1,2]. The algae can produce molecular hydrogen in the absence of sulfur under anaerobic conditions [1,3,4]. The terrestrial plants are the priority raw materials of the bioethanol production however the microalgae have lower lignin and hemicellulose content [5] and therefore would be more suitable raw materials than the terrestrial plants. Biogas can be produced from the microalgae by the anaerobic digestion [6]. The oil content of the algae can be extracted and converted into biodiesel using different catalysts and a fixed bed reactor described by Krohn et al. [7]. Biodiesel can be directly produced from the algal biomass as well [5]. This production method was demonstrated in detail earlier [8,9]. The biodiesel from algal biomass process can be accomplished more economically and environmental-friendly way when all the components and by-products of algae are effectively utilized including the pyrolysis oil and the pyrolysis gas of the algal residues. The thermoanalytical and the pyrolysis methods are useful techniques to determine the differences between the product distributions of biomass samples under various experimental conditions without separating the main fractions [10-13]. In this study thermogravimetry/mass spectrometry (TG/MS) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) measurements had been carried out to study the thermal decomposition mechanisms and product distribution of the microalgae sample with or without different mesoporous silica catalysts.

2. Materials and Methods

Production of deoiled algal cake (DAC)

The dried algal biomass was subjected to sonication in order to disrupt the algal cell wall. The extraction was performed using n-hexane in the Soxhlet extraction apparatus. After several cycles of run the concentrated oil sample was transferred into a flask and the solvent was evaporated using a rotary evaporator. The deoiled algae powder was washed by 60°C hot water during 2 hours in order to eliminate the main part of the water soluble organic and inorganic compounds of the sample.

Catalysts

Mesoporous silica catalysts (SBA-15 and FSM-16) were used to upgrade the thermal decomposition products of the deoiled algae powder.

TG/MS

The TG/MS system consists of a modified Perkin-Elmer TGS-2 thermobalance and a Hiden HAL quadrupole mass spectrometer. About 4 mg deoiled algae sample was measured in argon atmosphere at a flow rate of 140 ml min⁻¹. About 7-8 mg sample amount was applied using the algae with catalysts mixed in ratio 1:1. The samples were heated at a rate of

20°C min⁻¹ from 25 to 950°C in a platinum sample pan. The evolved products were introduced through a glass lined metal capillary heated at 300°C into the ion source of the mass spectrometer which was operated at a 70 eV electron energy.

Py-GC/MS

Approximately 3 mg deoiled algae powder was pyrolyzed at 600°C for 20 s in helium atmosphere using a Pyroprobe 2000 pyrolyzer interfaced to an Agilent 6890A/5973 GC/MS. The catalysts were placed in both sides of the sample in order to ensure that the evolved gas phase products can flow through to the catalyst bed. The pyrolysis products were separated on a DB-1701 capillary column (30 m × 0.25 mm, 0.25 μm film thickness). The GC oven was programmed to hold at 40°C for 4 minutes then increasing the temperature to 280°C (hold for 7 min) at a rate of 6°C min⁻¹. The mass range of m/z 14 – 500 was scanned by the mass spectrometer in an electron impact mode at a 70 eV.

3. Results and Discussion

TG/MS results

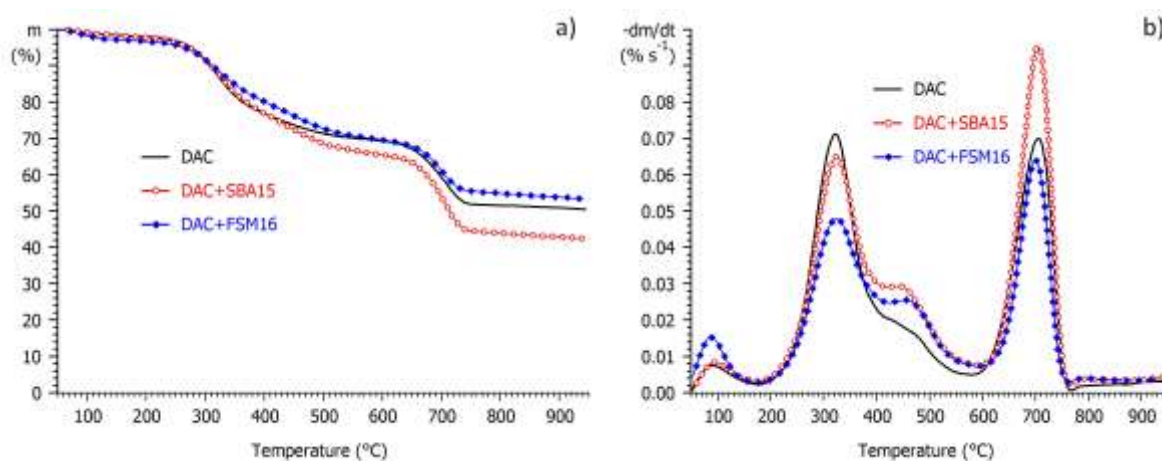


Figure 1 – Thermogravimetric (a) and differential thermogravimetric curves (b) of the deoiled algae cake (DAC) and the DAC mixed with SBA-15 and FSM-16 catalysts in the ratio 1:1 under argon atmosphere.

The TG and DTG curves of the deoiled algae cake (DAC) samples can be found in Figure 1. The algae contains at least 25 % oil [14] which was removed by the hexane extraction method after the sonication so the carbonaceous residue content of the deoiled sample is relatively high (Fig. 1a). The char content of the deoiled algae cake at 950°C decreased from 50 to 41 % using SBA-15 and increased slightly after mixing it with FSM-16. So the SBA-15 proved to be a better catalyst for making higher yield of the volatile decomposition products and lower yield of carbonaceous residue. The TG and DTG curves show that the thermal decomposition of the algae powders can be divided into three main degradation steps. The first peak on the DTG curves (Fig. 1b) between 50 and 180°C can be attributed to the evaporation of the adsorbed water. This conclusion can be proved by the mass spectrometric curve (m/z 18) of the water in the Figure 2a. The thermal decomposition of the organic compounds (e.g. carbohydrates, lipids, and proteins) starts at 200°C and ends at about 600°C in all samples. In the temperature range between 200 and 400°C the algae mixed with FSM-16 catalyst has a lower decomposition rate compared with the original sample, so the amount of the char is increased. The decomposition rate is not affected significantly by the SBA-15 catalyst. The mass loss of the remaining oil fraction of the algae takes place in the temperature range between 400 and 600°C. This can be clearly seen on the evolution profiles of the aliphatic hydrocarbon fragments e.g. vinyl (m/z 27 curves in Fig. 2b) and allyl (m/z 41 curves in Fig. 2c) fragments. These plots show the increased yields of the aliphatic fragment ions in this temperature range as well as at higher temperatures in case of vinyl groups similarly to the increased evolution of methane (not shown here). This is in agreement with the yields of the aliphatic compounds during the fast pyrolysis measurements (Fig. 3). The final decomposition step of DAC samples can be found between 600 and 800°C belonging to the transformation of inorganic carbonate content into carbon dioxide. This fact is supported by the CO₂ evolution on the mass spectrometric curve at m/z 44 (Fig. 2d). In presence of the SBA-15 catalyst the yield of the evolving carbon dioxide increased.

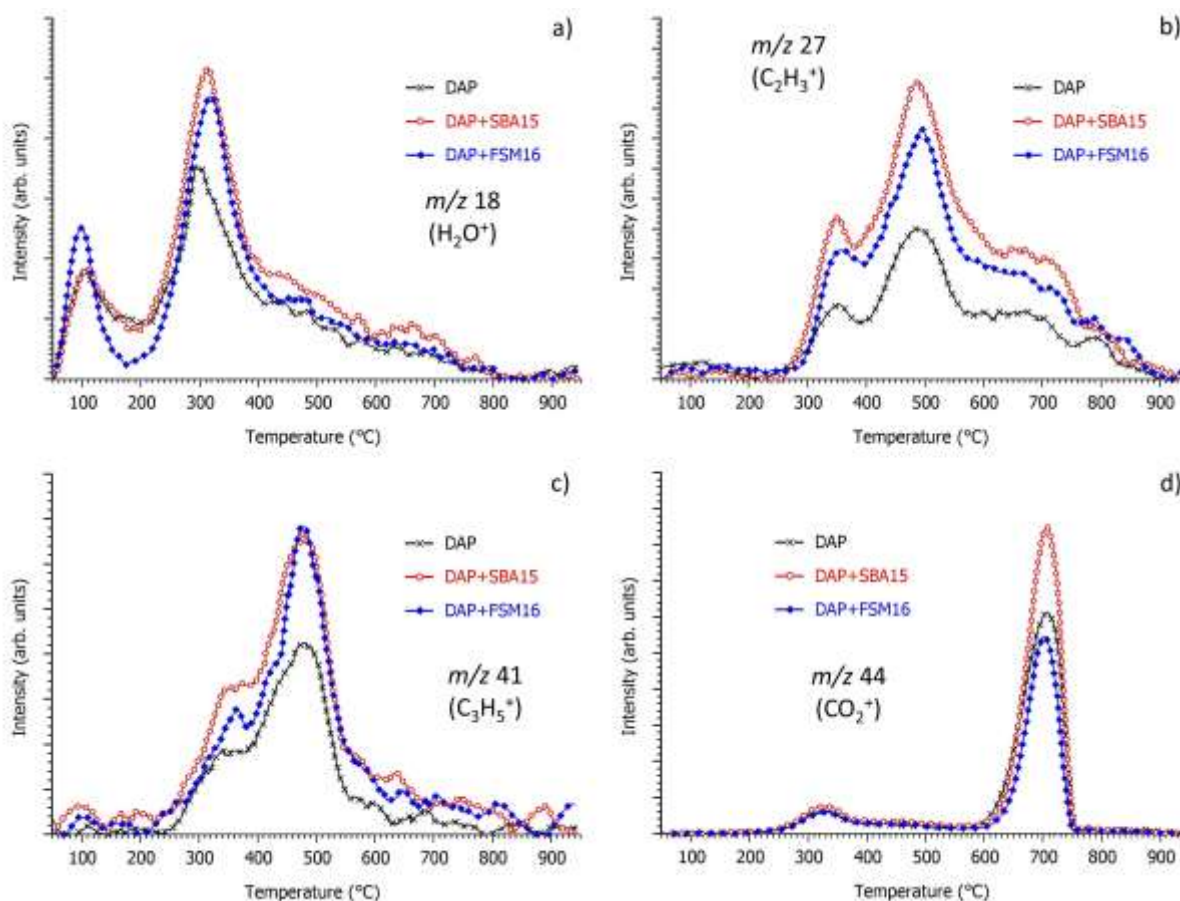


Figure 2 – Evolution profiles of the main decomposition products derived from DAC and DAC mixed with SBA-15 and FSM-16 catalysts: water (a), vinyl groups (b), allyl fragments (c) and CO₂ (d).

Py-GC/MS results

The pyrolysis-gas chromatography/mass spectrometry method was applied to identify changes in the pyrolysis product distribution using the catalysts. The temperature of the pyrolysis was chosen to 600°C because the TG and DTG curves (Fig. 1) show that the thermal decomposition of the organic part of the algae samples ended below this temperature. In Figure 3 the results of the Py-GC/MS measurements can be seen: the pyrograms of the native DAP sample (a), the DAP sample mixed with SBA-15 (b) and FSM-16 (c) catalysts. The catalysts were placed into the sample holder quartz tube at both side of the DAP sample so the evolved pyrolysis products go through the catalyst bed. The identification of the products is based on NIST mass spectral library and literature data [15,16].

The peaks at lower retention time just like carbon dioxide (peak #1) and water (peak #2) were formed by different decomposition reactions of many compounds. The acetic acid (peak #5) is a characteristic thermal decomposition product derived from the hemicellulose fraction. The furfural (peak #11) is evolved from hemicellulose and cellulose as well. The levoglucosan (peak #30) which is a dehydrated derivative of glucose is the main product of the thermal decomposition of cellulose under inert atmosphere. The yield of the levoglucosan is affected strongly by the catalysts, it was completely eliminated. The glucopyranose (peak #30) were transformed by the catalysts as well. The SBA-15 and the FSM-16 catalysts enhance the formation of ethanol (peak #3) and butanol (peak #4), respectively, among the evolved gas products of the deoiled algae. Alkane (peak #24) and alkene (peaks #8, #13, #15, #17, #22 and #25) decomposition products derived from the residual oil fraction of the algae. The yield of these aliphatic molecules is increased by a factor of 2 using the catalysts. The major compounds of the analytical pyrolysis of microalgae are the phenol (peak #16) and its derivatives (peaks #18, #20 and #21). These molecules are characteristic pyrolytic products of biomass materials originating from the lignin fraction. The yields of phenol and its derivatives decreased very strongly by using the catalysts. However the intensity of the alkyl aromatic compounds, e.g., toluene and styrene (peaks #6 and #10) are increased significantly in the presence of the FSM-16 catalyst.

The nitrogen containing decomposition products formed from the amino acid, alkaloid and chloroplast contents of the algae. The 4-methyleneproline (peak #33) is an amino acid derivative originating from the amino acid chains. Indole (peak #26) and its derivatives like 3-methyl-1H-indole (peak #28) formed by the fragmentation of tryptophan or indole alkaloids. The yield of these compounds is not affected by the presence of the catalysts. Pyrrole (peak #9) and its derivatives (peaks #12 and #14)

are the building parts of biologically important nitrogen containing compounds like chlorophylls, vitamins, vegetable hormones and amino acids (proline, hydroxyproline and tryptophan). The concentration of these chemicals increased using the catalysts. The isoindole derivatives (peaks #27 and #29) are only formed using the FSM-16 catalyst. Adenine (peak #32) is a purine derivative nucleobase originating from the ATP (adenosine triphosphate), NAD (nicotinamide adenine dinucleotide), and heritable materials RNA (ribonucleic acid) and DNA (deoxyribonucleic acid). The yield of aliphatic nitrile products (peaks #7 and #31) increased using the catalysts. The concentration of aromatic nitrile compounds (peaks #19 and #23) is not changed. There is a counter effect between the yield of hexadecane nitrile (peak #31) and hexadecane amide (peak #34). The catalysts promote the evolution of the aliphatic nitrile pyrolysis products contrary to the amide derivatives.

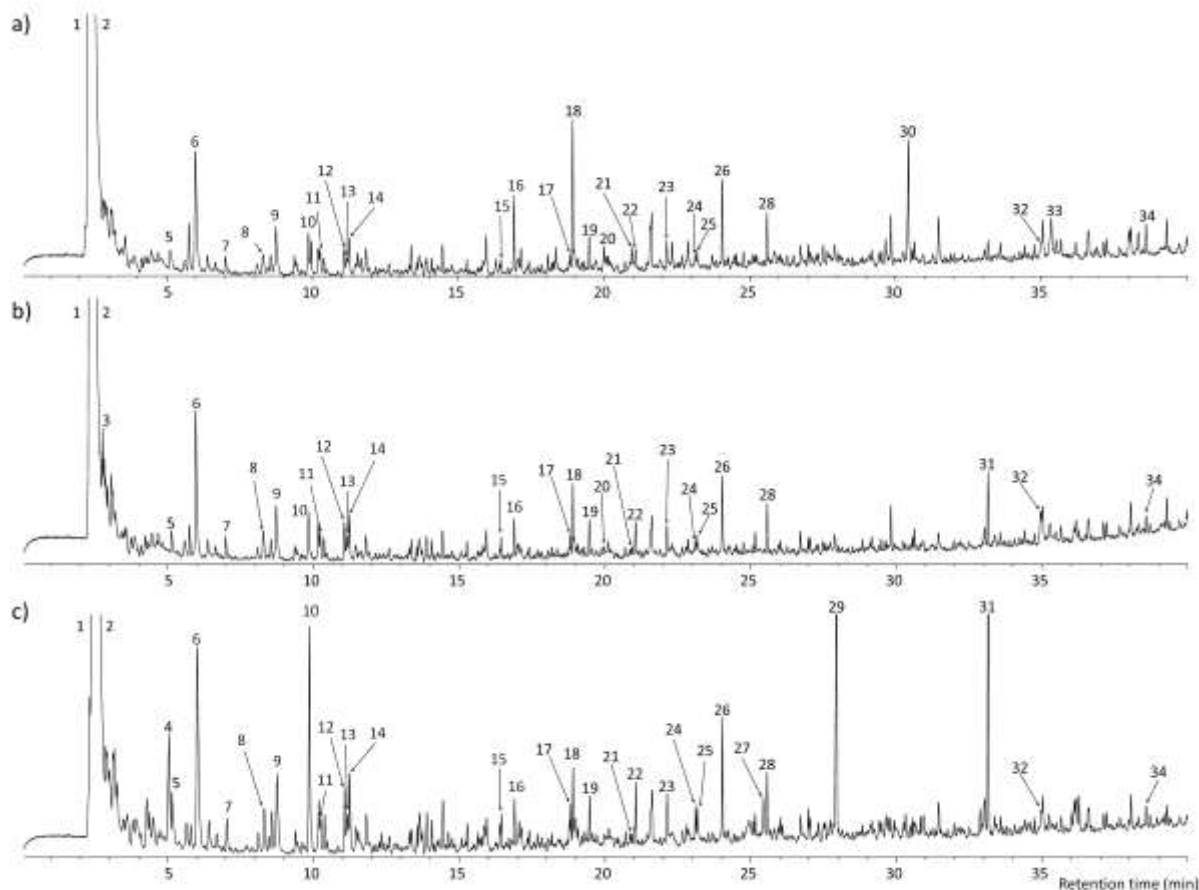


Figure 3 – Pyrolysis chromatograms of DAP (a), DAP mixed with SBA-15 (b) and FSM-16 (c) catalysts in a ratio 1:1 at 600°C. Numbered peaks are given in Table 1.

Table 1

The main decomposition products released in the Py-GC/MS experiment of DAC, DAC mixed with SBA-15 and FSM-16 catalysts. Peak numbers refer to the peaks in Fig. 3.

No.	Ret. Time (min)	Compounds	No.	Ret. Time (min)	Compounds
1	2,3	CO ₂	18	18,9	4-Methyl-phenol
2	2,4	H ₂ O	19	19,5	Benzyl-nitrile
3	2,8	Ethanol	20	20,0	2,4-Dimethyl-phenol
4	5,0	Butanol	21	20,9	4-Ethyl-phenol
5	5,2	Acetic acid	22	21,1	1-Tetradecene
6	6,0	Toluene	23	22,2	Benzenpropane nitrile
7	7,0	3-Methyl-butanenitrile	24	23,1	Pentadecane
8	8,3	1-Nonene	25	23,2	1-Pentadecene
9	8,7	Pyrrrole	26	24,0	Indole
10	9,9	Styrene	27	25,5	2-Methyl-1H-isoindole-1,3(2H)-dione
11	10,3	Furfural	28	25,6	3-Methyl-1H-indole
12	11,1	2-Methyl-1H-pyrrrole	29	28,0	1H-isoindole-1,3(2H)-dione
13	11,2	1-Decene	30	30,4	1,6-Anhydro-β-D-glucopyranose (Levoglucozan)
14	11,3	3-Methyl-1H-pyrrrole	31	33,2	Hexadecane nitrile
15	16,5	1-Dodecene	32	35,0	Adenine
16	16,9	Phenol	33	35,3	4-Methyleneproline
17	18,8	1-Tridecene	34	38,6	Hexadecane amide

4. Conclusions

In this study slow and fast pyrolysis methods (TG/MS and Py-GC/MS) were applied to identify the main decomposition products of the deoiled algal cake (DAC). Two different mesoporous silica catalysts (SBA-15 and FSM-16) were used in order to modify the evolved molecules in the gas phase. The yield of the carbonaceous residue formed at 950°C from the deoiled algae cake strongly decreased using SBA-15 and increased slightly after mixing it with FSM-16. So the SBA-15 proved to be a better catalyst for raising the yield of the volatile decomposition products and reducing the yield of the carbonaceous residue. As the pyrolysis results show ethanol and butanol were originated using the SBA-15 and the FSM-16 respectively. In case of both catalysts the levoglucosan yield of the algae cake powder decreased to zero. The glucopyranose derivatives adsorbed on the surface of the catalysts or they resolved. The presence of the catalysts during the fast pyrolysis measurements forced back the formation of the aromatic compounds and promoted the formation of the aliphatic decomposition products.

5. Acknowledgement

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6. References

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