Catalytic liquefaction of human feces over Ni-Tm/TiO₂ catalyst and the influence of operating conditions on products

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ABSTRACT

In this study, human feces were hydrothermal liquefied and converted into biocrude over Ni-Tm/TiO₂ catalyst. The influence of catalysts, reaction temperature, and holding time on the distribution of products and element content of biocrude was assessed. The biocrude yield increased to 53.16% with a reaction temperature of 330 °C, a holding time of 30 min, and adding Ni-Tm/TiO₂ catalyst while the liquefaction conversion peaked at 89.61%. The biocrude had an HHV of 36.64 MJ/kg and was similar to heavy crude oil. The biocrude is rich in fatty acid amides, esters, and oxygen-containing-only heteroatom-ring compounds as well as some nitrogen-containing heteroatom-ring compounds. The main gaseous products were CO₂, CH₄, and C₂H₆. Hydrothermal liquefaction over Ni-Tm/TiO₂ catalyst could be a potential method to handle human excrement treatment and produce biofuel.

1. Introduction

An average adult human generates about 200 g of wet feces every day [32]. At present, 982 million of people still use open defecation while more 2.3 billion of people lack access to improved sanitation worldwide [39]. The human feces are rich in organic matters, parasite, and pathogenic bacteria. As the biochemical solid waste from human excretion, feces not only spread diseases burden but also show negative impacts on the environment by contaminating the water bodies, soils, and food sources [29]. Nevertheless, the human feces still contain various abundant chemical element to produce the valuable fertilizer and fuel. Therefore, the human excrement could be used as a renewable resource and energy [14,22].

Traditional human feces utilization methods were universally applied through the history. For example, the composting has proved to be effective for killing both parasite and pathogenic bacteria while the anaerobic digestion is widely used for biogas production. However, these technologies require a long stabilization time to finish the biological treatment process, need additional treatment site, cause the unpleasant stink, and result in the derivative pollution from treatment. In comparison, the thermochemical process is a much faster and cleaner way to handle these human feces [12,13,27,44]. Among various thermochemical methods, hydrothermal liquefaction (HTL) operates at conditions of a temperature of 200–350 °C and a pressure of 5–20 MPa, which is milder than that in pyrolysis and gasification [7,17,47]. Meanwhile, the HTL directly converts the wet biomass into biocrude without removing the water in biomass feedstock. Comparing with incineration and pyrolysis, the HTL method could save the operating cost from additional drying operation. Moreover, it should be noted that HTL process could kill pathogens at high temperature while producing the biocrude fuel. Therefore, great attention has been drawn to this research topic.

Previous studies showed that swine manure and human feces could be converted into biocrude, with a biocrude yield around 20–40% [9,18,40,41]. However, the nitrogen (N), sulfur (S) and oxygen (O) content in biocrude are much higher than that in petroleum. The higher heteroatom (N, S, and O) content would cause catalyst poisoning or facility corrosion in biocrude refining for high-quality aircraft fuel. Thus, appropriate catalysts should be introduced into the HTL process to increase the biocrude yield or improve the biofuel properties. Various catalysts, such as alkalis, acids, transition metal oxides and noble metals were introduced into the HTL of other kinds of biomass. These catalysts showed the influence on the liquefaction conversion, biocrude yield and biocrude quality [16,21,30,43,46]. To the best of our knowledge, little information is available regarding the HTL of human feces, especially for catalytic liquefaction. In recent research, we found out that rare-earth-element and nickel-based TiO₂ catalyst greatly improved the HTL of high-protein-content microalga Spirulina [36]. This study convinced us that rare earth element and nickel supported on TiO₂ catalyst should behave well in the application in HTL of human feces which contain plenty of protein. We hope this study could fill the research gap in catalytic HTL of human feces.
Catalytic HTL of human feces could reduce the pollution from the excrement to the environment and provide an added value for the outlet of human feces treatment. In this study, we would focus the catalytic liquefaction of human feces over Ni-Tm/TiO₂ for producing biocrude and treating human feces. We also determined the influence of reaction temperature and holding time on the yields of products.

2. Materials and methods

2.1. Feedstock and reagents

Fresh human feces were collected from an aqua privy located in Xingshou Village, Nanzhuang Town, Changping District of Beijing, China. The feedstock was well stirred and then sealed and stored in cold storage at −12 °C in a freezer. The samples were transferred into a refrigerator overnight at 4 °C and thawed at 30 °C for 12 h before use. The characteristics of the human feces were presented in Table 1. The TiO₂ was acidized by 1.0 mol/L nitric acid for 4 h, washed with deionized water and then dried at 105 °C for 24 h and then weighed. The liquid phase mixture was separated into the aqueous product and the DCM-soluble phase product in a separating funnel. The DCM-soluble phase product was evaporated under vacuum (60 °C, 0.01 MPa) to remove the DCM. The obtained black sticky liquid was used as the biocrude and weighted.

2.2. Preparation of bimetallic catalyst

The catalyst preparation was based on our previous research [36]. Wet impregnation method was applied to prepare the catalyst precursor. TiO₂ and the amounts of Tm(NO₃)₃·6H₂O, Ni(NO₃)₂·6H₂O, TiO₂ powder, and HNO₃ were all of the pure analytical grades and purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Nitrate neodinium, lanthanum, and Cerium of analytic grade pure were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Deionized water was used in the experiment. All the reagent were used without further purification.

2.3. HTL process and product separation

The HTL process was carried out in a stainless 316 steel batch reactor (GS-0.6, Weihai Chemical Machinery Co., Ltd, China) with a volume capacity of 600 mL and heated by an external electrical furnace. The reactor is designed to a maximum temperature of 400 °C and pressure of 30 MPa. Human feces processed by HTL was carried out based on 300 g with/without the catalyst (based on 10% of dry weight of feedstock). The feces and catalyst mixture was stirred with a magnetic stirring and sealed in the reactor. Pure nitrogen was pressurized into the reactor headspace to provide an oxygen-free condition. The reactor was heated to a pre-set temperature, which was defined as the reaction temperature. Operating parameters, including reaction temperature and holding time, were investigated in the range of 250–350 °C and 0–720 min, respectively.

After holding for some time, the reactor was cooled down to room temperature. The pressure in the reactor was released from the gas outlet tube, and the gases were collected by a gas bag and weighted by an Analytical Balance (ME204T/02, METTLER TOLEDO, Switzerland). The gas bag was pre- vacuumized and weighted. 400 mL of Dichloromethane (DCM) was used to wash the reactor and the stirring head. The collected mixtures (containing the aqueous product, biocrude, solid residue, and DCM) were separated into the liquid phase mixtures and solid residue by vacuum filtration. The solid residue was washed for at least three times with 50 mL of DCM to remove other products. The solid residues were dried in a drying oven at 105 °C for 24 h and then weighed. The liquid phase mixture was separated into the aqueous product and the DCM-soluble phase product in a separating funnel. The DCM-soluble phase product was evaporated under vacuum (60 °C, 0.01 MPa) to remove the DCM. The obtained black sticky liquid was defined as the biocrude and weighted.

2.4. Calculation and analytic methods

All the calculated results listed are the average values from experimental results performed at least three times and all by dry ash free (daf) weight. Eqs. (1)–(5) calculated the yield of biocrude, solid residue, gaseous products, aqueous products and the liquefaction conversion, respectively.

Biocrude yield \( (Y_{bi}, \%) = \frac{M_{bi}}{M_{F(daf)}} \times 100 \) (1)

Gaseous product yield \( (Y_{G}, \%) = \frac{M_{G}}{M_{F(daf)}} \times 100 \) (2)

Table 1
Proximate and ultimate analysis of feedstock.

| Parameters          | Human feces | Sludge [35] | Nannochloropsis [34] |
|---------------------|-------------|-------------|----------------------|
| This study          |             |             |                      |
| Proximate analysis (%) |            |             |                      |
| TS (Total solid)    | 15.13 ± 1.93| 19.6 ± 3.8  | 15.48                |
| Ash                 | 9.28 ± 0.42 | 17.0 ± 1.3  | 23.01                |
| Biochemical analysis (%) |          |             |                      |
| Protein             | 45.28 ± 1.94| –           | 37.84                |
| Lipid               | 13.50 ± 1.10| –           | 8.01                 |
| Carbohydrate        | 31.94 ± 0.89| –           | 31.14                |
| Organic element analysis (%) |      |             |                      |
| C                   | 50.51 ± 1.06| 42.4 ± 1.3  | 46.68                |
| H                   | 6.75 ± 0.31 | 6.9 ± 0.9   | 6.85                 |
| O                   | 35.76 ± 0.90| 43.1 ± 3.1  | 37.60                |
| N                   | 6.05 ± 0.49 | 5.9 ± 1.0   | 8.05                 |
| S                   | 0.53 ± 0.02 | 1.7 ± 0.5   | 0.81                 |

* Based on dry biomass.
* Calculated by difference.
Solid residue yield \( (Y_{\text{s}}, \%) = \frac{M_{\text{d}} - M_{\text{a}} - M_{\text{c}}}{M_{\text{d}}(\text{daf})} \times 100 \)  

Aqueous product yield \( (\%) = 100 - Y_S - Y_T - Y_G \)  

Liquefaction conversion \( (\%) = 100 - Y_S \)  

where MB, MF (daf), MG, MA, and MC were the weight of biocrude, human feces (based on the dry ash-free weight), gaseous products, ashes in feces and catalyst. The liquefaction conversion represented the percentage of the organic matters in feces liquefied into non-solid phase product and was set to evaluate the treatment level of human feces.

The HHV of human feces and biocrude were calculated according to the Gumnz correlation (Eq. (6)) [6]:

\[
\text{HHV (MJ/kg)} = 0.3403 \times C + 1.2432 \times H + 0.0628 \times N + 0.1909S - 0.0984O
\]

where C, H, O, N and S were the weight percentage of carbon, hydrogen, oxygen, nitrogen, and sulfur in the feedstock and biocrude, respectively. Organic element content of the product was detected with an elemental analyzer (CE-400, Exeter Analytical, Inc. USA). The oxygen content was calculated by difference.

The energy recovery (ER) was used for evaluating the energy efficiency and calculated by Eq. (7):

\[
\text{ER (\%)} = \frac{\text{Biocrude yield} \times \text{HHV}_{\text{biocrude}}}{\text{HHV}_{\text{human feces}}}
\]

The organic composition of biocrude was analyzed with a gas chromatography-mass spectrometry (GC-MS, QP2010, Shimadzu Co., Tokyo, Japan). A Varian DB-5 column (30 m × 0.25 mm × 0.25 μm) was the GC column, and helium was the carrier gas. The ion source temperature, injection temperature, and interface temperature were 200, 250 and 320 °C, respectively. The mass spectrometer was operated in positive electron impact mode (EI) at 70 eV with a scan range of m/z from 20 to 650. All chromatogram peaks in spectra were compared with chromatography-mass spectrometry (GC-MS, QP2010, Shimadzu Co., μm 0.45 in positive electron impact mode (EI) at 70 eV with a scan range of 200, 250 and 320 °C, respectively. The mass spectrometer was operated for 20 min. afterward increased to 250 °C at the same heating rate and maintained for 20 min.

The gaseous product analysis was carried out with an Agilent Technologies model 7820A gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The GC column was a 15 ft × 1/8 in. i.d. stainless steel column packed with 60 × 80 mesh Carboxen 1000 (Sperlco). Argon was used as the carrier gas. Mole fractions of the gaseous products were calculated based on the calibration curves, which was determined by the analysis of gas standards with known compositions.

3. Results and discussion

3.1. Effect of different catalysts in the liquefaction process

The introduction of catalysts into the HTL process could increase the biocrude yield and improve the biocrude quality. The preliminary experiments of feces HTL with different Ni-M/TiO2 catalyst (M = Tm, Nd, Ce, and La) suggested that only the Ni-Tm/TiO2 showed a positive effect on the HTL process (Fig. S1). Further discussion about the catalytic effect of the Nd, Ce, and La catalysts is beyond our research scope. Fig. 1 showed the effect of different catalyst conditions on the liquefaction process. The operating conditions were a reaction temperature of 300 °C, a holding time of 30 min, a biomass loading of 20% and with/without a catalyst loading of 10%. The process without catalyst was labeled as the blank experiment.

As shown in Fig. 1, the distribution of product yields was influenced by the introduction of catalysts. Adding Ni-Tm/TiO2 catalyst increased the biocrude yield from 41.57% to 46.09% while Ni/TiO2, Tm/TiO2, and TiO2 demonstrated no significant effect on biocrude yields. Compared with the direct liquefaction of human feces in the literature, our biocrude yield was much higher, which could be due to the difference in feedstock composition [18]. According to further element analysis in Table 2, the Ni-Tm/TiO2 catalyst increased the concentration of carbon and hydrogen element by 10.39% and 4.64% in biocrude, respectively. The catalytic HTL process with Ni-Tm/TiO2 converted more than 64% of the carbon and 70% of the hydrogen in human feces into biocrude. Moreover, the H/C atom ratio of 1.54 indicated that the obtained biocrude was similar to heavy oil [20]. Meanwhile, the sulfur content in biocrude was reduced by 22.58% by adding Ni-Tm/TiO2 catalyst. This reduction was mainly attributed to the desulfuration of Ni catalyst, which was observed in the HTL of microalgae [8,36]. The slight increase of oxygen content could come from the conversion of high-oxygen-content carbohydrate with the introduction of Tm and TiO2 catalyst composition. According to previous research, the carbohydrate needs higher active energy to be liquefied into biocrude and usually remained as the form of solid matters in the direct liquefaction process [33]. However, the hydrocarbons like celluloses could be efficiently converted into biofuel over Tm catalyst and TiO2 catalyst [25,37,38]. That was also corresponding to the decrease of solid residue yield by 59.03% after the dosage of Ni-Tm/TiO2 catalyst. That was also corresponding to the decrease of solid residue yield by 59.03% after the dosage of Ni-Tm/TiO2 catalyst. Adding Ni-Tm/TiO2 catalyst showed a positive influence on the improvement of liquefaction conversion, compared with the blank experiment.

The increased gaseous product yield indicated that Ni-Tm catalyst catalyzed more biomass into small gas molecules. The catalytic effect might be mainly attributed to the catalysis of nickel, which was the catalyst for the gas yield improvement in the HTL and the gasification of microalgae [3,10,23]. This improvement would be pleasing because

| Catalyst | Element composition (wt.%) | H/C | HHV (MJ/kg) | ER (%) |
|----------|----------------------------|------|-------------|--------|
| Blank    | 71.10 9.79 11.31 7.49 0.31 0.31 | 1.65 | 35.78 | 66.77 |
| TiO2     | 66.13 8.05 16.62 8.67 0.53 0.53 | 1.46 | 31.52 | 58.69 |
| Ni/TiO2  | 68.39 8.76 14.44 7.96 0.45 0.45 | 1.54 | 33.33 | 63.50 |
| Tm/TiO2  | 67.14 9.02 15.46 8.13 0.25 0.25 | 1.61 | 33.10 | 61.41 |
| Ni-Tm/TiO2 | 71.79 9.24 10.45 8.28 0.24 0.24 | 1.54 | 35.45 | 73.34 |

ER: energy recovery.
Triplicate was conducted for element analysis, the relative standard deviation value was less than 1%, and only average value was presented.

a Calculated by difference.
some enhanced decarboxylation reactions can reduce the oxygen content in the form of CO₂ with acceptable carbon loss. The CO₂ was detected and in the gaseous product analysis in Section 3.4. The reaction temperature, as the most important operating parameter, showed a conclusive effect on the yield of biocrude and products of other phases [2]. Fig. 2(b) presented the effect of holding time on catalytic HTL of human feces over Ni-Tm/TiO₂ catalyst. The higher reaction temperature could be conducive to the biomass gasification and might enhance the transformation from biocrude to aqueous products [4,33].

3.2.1. Effects of temperature on catalytic HTL of human feces over Ni-Tm/TiO₂ catalyst

The reaction temperature, as the most important operating parameter, showed a conclusive effect on the distribution of the product [1]. As shown in Fig. 2(a), with the reaction temperature increasing from 250 to 330 °C, the biocrude yield gradually increased from 17.03% at 0 min much higher than that in other literature [11]. According to our experiment records, the heating of the reactor from 250 to 330 °C took around 30 min, which means that the experiment at 330 °C and 0 min should be regarded as an experiment holding for 30 min at a temperature between 250 and 330 °C. The solid residue yield of 17.03% at 0 min was lower than the biocrude yield of 39.44% without catalyst (from 29.80 to 15.27%) was close to the rapid growth of the yield of aqueous products (from 20.13 to 31.30%). When the reaction temperature was lower than 290 °C, the main transformation should be the decomposition of solid matters and the formation of aqueous products. However, in the temperature range from 290 to 330 °C, the formation of the biocrude and gaseous products from solid residues and aqueous products should be the protagonist among the liquefaction reaction pathways. Further increase of the temperature from 330 to 350 °C lowered the biocrude yield to 44.86%. Meanwhile, the yield of solid residues remained unchanged almost while both the yields of gaseous and aqueous products increased. The disappeared biocrude should be transferred into gaseous or aqueous products, because the higher reaction temperature could be in favor of the biomass gasification and might enhance the transformation from biocrude to aqueous products [4,33].

Further element analysis presented in Table 3 showed a steady increase of carbon and hydrogen contents with the temperature increasing. Raising reaction temperature could be conducive to the carbon and hydrogen, as the main element in the hydrocarbon fuel, transferring from feces to biocrude. The higher heat values (HHV) of biocrude samples suggested that raising reaction temperature led to a higher HHV and the highest HHV was obtained at 350 °C (36.76 MJ/kg). However, the higher reaction temperature could be a challenge to the equipment life and require a higher operating cost for more energy input. Taken the similar HHVs at 330 (36.64 MJ/kg) and 350 °C into the calculation, the appropriate reaction temperature should be 330 °C, which led to the highest energy recovery of 87.42%.

3.2.2. Effect of holding time on catalytic HTL of human feces over Ni-Tm/TiO₂ catalyst

Holding time is defined as a period for the reactor to react at a maximum temperature, excluding the heating and cooling times [42]. As an important operating parameter, the length of holding time is believed to be closely linked to the yield of biocrude and products of other phases [2]. Fig. 2(b) presented the effect of holding time on the HTL of human feces over Ni-Tm/TiO₂ catalyst. The single factor experiments were carried out at 330 °C, a Ni-Tm/TiO₂ catalyst loading of 10 wt% and with a holding time range from 0 to 720 min. As shown in Fig. 2(b), the biocrude yield gradually increased from 43.48% to 53.16% when holding time extended from 0 to 30 min. It should be noted that the obtained biocrude yield with a holding time of 0 min much higher than that in other literature [11]. According to our experiment records, the heating of the reactor from 250 to 330 °C took around 30 min, which means that the experiment at 330 °C and 0 min could be regarded as an experiment holding for 30 min at a temperature between 250 and 330 °C. The solid residue yield of 17.03% at 0 min suggested the incomplete conversion of solid organic matter into products of other phases (liquid or gas) without enough reaction time. With further extension of holding time to 720 min, the biocrude yield gradually reduced to 46.25%. Meanwhile, the yield of solid residue and the aqueous product showed unchanged almost in this time range.
Triplicate was conducted for element analysis, the relative standard deviation value was less than 1%, and only average value was presented.

**ER**: energy recovery.

### 3.3. Molecular characterization of biocrude from catalytic liquefaction

The GC-MS analyzed the biocrude samples obtained at 330 °C and 30 min, and the NIST library identified the main chemical compounds. It should be noted that some low-molecular-weight compounds could get lost during the evaporation process for obtaining the biocrude, while the high-molecular-weight compounds could not volatilize, then get lost during the evaporation process for obtaining the biocrude, but the results could provide us some useful information about obtained biocrude. When identifying the biocrude, only components were selected by GC-MS. Thus, we have simplified the discussion, the identified results were listed in Table 4. To simplify the discussion, the identified compounds were classified into six groups: esters, fatty acids, O-containing-only hetero-atom compounds (OH), amides, N-and-O-containing hetero-atom compounds (NOH), N-containing-only heterocyclic compounds (NH).

As shown in Fig. 3, the biocrude produced without catalyst had the fatty acids as the uppermost compounds, followed by esters, fatty acid amides. There were a few NHs and OHs in this biocrude sample, and the identification showed the absence of the NOHs. By adding Ni-Tm/TiO₂ catalyst, the relative content of esters and fatty acid compounds decreased by 27.51% and 84.27%, respectively. Meanwhile, the relative content of fatty acid amides, which was the reaction product of fatty acid and small molecule amine, increased by 76.71%. The amines, as the decomposition product of amino acid, came from the hydrolysis of protein [5]. As both the products from fatty acids, there was an obvious competitive relationship between esters and fatty acid amides and the esterification reaction might be probably restrained by adding the Ni-Tm/TiO₂ catalyst. According to Fig. 3 and Table 4, the relative content of NH and OH compounds in the catalytic biocrude sample increased from 2.03 and 1.45 to 7.73 and 23.48%, respectively. Besides, the NOH compounds appeared by adding the Ni-Tm/TiO₂ catalyst. Some of these heterocyclic compounds could come from the Maillard reaction

| Temperature (°C) | Holding time (min) | Element content (wt.%) | C | H | O* | N | S | H/C | HHV (MJ/kg) | ER (%) |
|-----------------|--------------------|------------------------|---|---|----|---|---|-----|-------------|-------|
| Blank           | 30                 | 73.10                  | 9.79 | 11.31 | 7.49 | 0.31 | 1.65 | 35.78 | 66.76 |
| 330             | 30                 | 72.83                  | 9.84 | 10.60 | 6.44 | 0.29 | 1.62 | 36.43 | 64.48 |
| With 10% catalyst | 250 | 68.69                  | 8.69 | 13.45 | 8.64 | 0.53 | 1.52 | 33.50 | 64.08 |
|                 | 270 | 70.13                  | 8.73 | 13.35 | 7.34 | 0.45 | 1.49 | 33.95 | 66.72 |
|                 | 290 | 70.58                  | 8.30 | 13.81 | 6.95 | 0.36 | 1.41 | 33.48 | 67.37 |
|                 | 300 | 71.79                  | 9.24 | 10.45 | 8.28 | 0.24 | 1.54 | 35.45 | 73.34 |
|                 | 310 | 71.56                  | 9.74 | 11.66 | 6.82 | 0.22 | 1.63 | 35.78 | 77.42 |
|                 | 330 | 72.86                  | 9.83 | 9.43  | 7.42 | 0.46 | 1.62 | 36.64 | 87.42 |
|                 | 350 | 72.89                  | 9.89 | 9.23  | 7.48 | 0.51 | 1.63 | 36.76 | 74.01 |
|                 | 330 | 0                     | 64.00 | 8.67  | 17.03 | 9.44 | 0.86 | 1.63 | 31.64 | 57.48 |
|                 | 330 | 120                   | 73.48 | 10.02 | 8.94  | 7.13 | 0.43 | 1.64 | 37.11 | 85.88 |
|                 | 330 | 360                   | 73.47 | 10.13 | 8.15  | 7.92 | 0.33 | 1.65 | 37.35 | 80.86 |
|                 | 330 | 720                   | 73.68 | 10.37 | 8.43  | 7.05 | 0.47 | 1.69 | 37.67 | 78.19 |

**Table 3**

Analysis of biocrude samples from various HTL operating conditions with Ni-Tm/TiO₂ catalyst.

**Table 4**

Tentative identities and area percentage of major peaks in GC-MS for biocrude samples from HTL of human feces at 330 °C for 30 min and with and without 10 wt% Ni-Tm/TiO₂.

| Retention time (min) | Name | Molecular formula | Relative abundance (area %) |
|----------------------|------|-------------------|-----------------------------|
| 3.49                 | Methylpyrazine | C₅H₅N₂ | 0.33 | 2.07 |
| 4.38                 | 2-Methyl-2-cyclopenten-1-one | C₅H₉O | 1.87 | – |
| 4.41                 | 2,3-Dimethylpyrazine | C₅H₈N₂ | 0 | 1.95 |
| 5.39                 | 2-Ethyl-5-methylpyrazine | C₆H₁₀N₂ | 0.84 | 2.24 |
| 5.69                 | 2-methyl-5-ethylpyridine | C₇H₁₂N | 0 | 1.47 |
| 6.27                 | 2,6-Diethylpyrazine | C₇H₁₀N₂ | 0.54 | – |
| 7.10                 | 2,3-Diethyl-5- methylpyrazine | C₈H₁₂N₂ | 0.15 | – |
| 8.64                 | (E)-1-cycloheptenylpyrrolidinone | C₁₁H₁₇N₂O₆ | – | 3.03 |
| 10.10                | 2,2,2-(propane-1,3-diylbis (azanethiol))tetraacetic acid | C₁₀H₁₉N₂O₈ | – | 2.85 |
| 13.04                | 1-Dodecanamide, N,N- butylpiperazine-2,5-dione | C₁₂H₁₄N₂O₂ | 7.03 | 1.66 |
| 14.04                | (35,6S)-3,6-di-sec- butylpiperazine-2,5-dione | C₁₂H₁₄N₂O₂ | – | 2.39 |
| 14.4                 | Palmitic acid | C₁₅H₂₇O₂ | 31.1 | 4.89 |
| 14.5                 | Phthalic acid, 3-methylbutyl undecyl ester | C₁₅H₂₈O₂ | 6.55 | 1.12 |
| 14.71                | Ethyl palmitate | C₁₇H₃₃N₂O₂ | 3.99 | 0.82 |
| 15.08                | Phorbol | C₁₆H₂₇O₂ | 1.45 | 1.41 |
| 16.86                | (E)-octadec-1-enyl isocyanate | C₁₈H₃₆N₂O₂ | – | 1.76 |
| 17.02                | Palmitamide | C₁₈H₃₄NO | 4.85 | 12.66 |
| 18.05                | 1-Dodecanamide, N,N- dimethyl- | C₁₈H₃₄NO | 5.51 | – |
| 19.48                | (Z)-9-Octadecenamide | C₁₉H₃₈N₂O₂ | 2.82 | 10.63 |
| 22.08                | Dioctyl phthalate | C₂₀H₄₂O₄ | 1.64 | 8.42 |
| 29.68                | Cholest-5-en-3-ol | C₂₀H₃₂O | – | 19.22 |

**ER** = energy recovery.

Triplet was conducted for element analysis, the relative standard deviation value was less than 1%, and only average value was presented.

* Calculated by difference.

However, to obtain the gaseous product yield was positively correlated with the length of holding time. The highest gas yield (21.47%) was obtained with a holding time of 720 min. It seems that holding for a long time gave the biomass and other products enough time to crack into small gaseous molecules [1]. Element analysis presented in Table 3 showed that a longer holding time resulted in a slight increase of element content of carbon and hydrogen, H/C atom ratio and HHV of biocrude in general. However, longer holding time (more than 30 min) led to a decrease in energy recovery from the highest at 30 min (87.42%) to 78.19% at 720 min. Moreover, the lengthened holding time also consumed more energy for heating. Therefore, a holding time of 30 min is appropriate for HTL of human feces over Ni-Tm/TiO₂ catalyst.
between the protein and carbohydrate [45]. This inference was corresponding to the catalytic effect on the carbohydrate conversion with Tm and TiO2 catalyst composition mentioned in Section 3.1. The identification results also indicated that the Ni-Tm/TiO2 catalyst must enhance the formation of compounds with more rings (like cholesterol) and the condensation to larger molecules (like phthalate, piperazine, and tetraacetic acid) in the hot pressure water [15,24,26,31]. The condensation reaction from smaller molecules to larger compounds could improve the biocrude yield, and lead to the deoxygenation, deamination, and desulfuration of biocrude. This conjecture was associated with the changed product distributions and element contents by adding Ni-Tm/TiO2 catalyst in Section 3.1.

3.4. Distribution of gaseous products

The identification and relevant fractions of gaseous products formed from HTL of human feces over Ni-Tm/TiO2 catalyst were discussed in this section. The most obtained compounds were N2 (initially loaded atmosphere gas), CO2, CO, CH4, C2H6, C3H8. Some unsaturated products like C2H4 and C3H6 were detected without catalyst application, and these ethylene and propene were likely hydrogenated to C2H6 and C3H8 during catalytic HTL. No H2, NH3, or NO2 was found out in all HTL experiments. The gas compositions were calculated on an N2-free basis.

As shown in the Fig. 4, the distribution of gaseous product was affected by the extension of holding time and the increase of reaction temperature. CO2 was always with the highest amount under all conditions, as what demonstrated in the HTL of microalgae and soy protein concentration [8,19]. The content of methane and ethane were the second and the third highest in relevant content. Fig. 4(a) shows the effect of holding time on the gaseous product distribution from HTL of human feces at 330 °C. The relevant content of methane and ethane increased while there was less CO2 with longer holding time until the holding time was longer than 120 min. Further extension of holding time lead to an almost unchanged relevant mole percentage of gases. Therefore, the gaseous product composition showed a weak influence from reaction time. Meanwhile, Fig. 4(b) suggested that the reaction temperature had a more strong influence on the gas composition. With the increase of temperature, the proportion of CH4 decreased, and the HTL process produced more C2H6. Moreover, the percentage of CO2 and C3H8 also increased slightly. This trend was similar to the gasification of biomass into small molecular alkane at a higher temperature with the nickel catalyst and various and complex organic reactions, like steam reforming, water-gas shift, methanation, and decarboxylation, were taken place during the HTL process [8,10].

4. Conclusion

Human feaces were treated by hydrothermal liquefaction over Ni-Tm/TiO2 catalyst. The best liquefaction conditions were at 330 °C and holding for 30 min, and the highest biocrude yield and liquefaction conversion were 53.16% and 89.61%, respectively. The Ni-Tm/TiO2 catalyst improved the biocrude yield by 34.79% and provided an energy recovery of 87.42%. Fatty acid amides, oxygen-containing-only heteroatom compounds, and esters were the main compounds in biocrude. CO2, CH4, and C2H6 were the main gaseous products from catalytic liquefaction process. Catalytic hydrothermal liquefaction over Ni-Tm/TiO2 could be a potential method for the treatment and conversion of human feces.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.enconman.2017.11.081.

References

[1] Akhtar J, Amin NAS. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. Renew Sustain Energy Rev 2011;15(3):1613–24.
[2] Anastasakis K, Ross AB. Hydrothermal liquefaction of the brown macro-alga Laminaria saccharina: effect of reaction conditions on product distribution and composition. Bioreourc Technol 2011;102(7):4876–83.
[3] Ayus T, Abd Rahman NA, Sunna A. Catalytic pyrolysis of Tetraselmis and biocrude microalgae by nickel ceria based catalysts for hydrocarbon production. Energy 2016;103:205–14.
[4] Brown TM, Duan PG, Savage PE. Hydrothermal liquefaction and gasification of nannochloropsis sp. Energy Fuels 2010;24:3693–46.
[5] Changi SM, Faeth JL, Moore N, Savage PE. Hydrothermal reactions of biomolecules relevant for microalgae liquefaction. Ind Eng Chem Res 2015;54(47):17133–58.
[6] Channiwala SA, Parikh PP. A unidirectional reactor for estimating HHV of solid, liquid and gaseous fuels. Fuel 2002;81(10):1051–63.
[7] Chen Y, Wu YL, Hua DR, Li C, Harold MP, Wang JL, et al. Thermochemical conversion of low-light microalgae for the production of liquid fuels: challenges and opportunities. RSC Adv 2015;5(24):18673–701.
[8] Duan PG, Savage PE. Hydrothermal liquefaction of a microalg with heterogeneous catalysts. Ind Eng Chem Res 2011;50(1):52–61.
[9] Elko U, Ross AB, Camargo-Valero MA, Williams PT. A comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing of microalgae, manure and digestate. Bioreourc Technol 2016;200:951–60.
[10] Elliott DC. Catalytic hydrothermal gasification of biomass. Biofuels, Bioprod Bioref 2008;2(3):254–65.
[11] Faeth JL, Valdez PJ, Savage PE. Fast hydrothermal liquefaction of nannochloropsis sp to produce biocrude. Energy Fuels 2013;27(3):1391–9.
[12] Fonts I, Gea G, Azaara M, Abrego J, Arauzo J. Sewage sludge pyrolysis for liquid production: a review. Renew Sustain Energy Rev 2012;16(5):2781–805.
[13] He BJ, Zhang Y, Funk TL, Ruskowski GL, Yin Y. Thermochemical conversion of swine manure: an alternative process for waste treatment and renewable energy production. Trans ASABE 2004;43(6):1827–33.
[14] Heinonen-Tanski H, van Wijk-Sijbersma C. Human excreta for plant production. Bioreourc Technol 2005;96(4):403–11.
[15] Islam MN, Kanoeki K, Kobayashi K. Reaction of amino acids in a Supercritical water-processing of microalgae using alkali and organic acids. Fuel 2010;89(9):2234–43.
[16] Lindsay JR, Liston MB, Kooistra S, Schofield JL. Compositions of human excreta over Transition metal supported TiO2 catalysts. Bioresour Technol 2017. http://dx.doi.org/10.1016/j.biortech.2017.11.051.
[17] Lu JW, Zhang JR, Zhu ZB, Zhang YH, Zhao Y, Li RR, et al. Simultaneous production of bio-oil and recovery of nutrients and metals from human feces via hydrothermal liquefaction. Energy Fuels 2015;29(2):150–6.
[18] Rose AL, Ross AB, Camargo-Valero MA, Williams PT. A comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing of microalgae, manure and digestate. Bioreourc Technol 2016;200:951–60.
[19] Ross AB, Biller P, Kubacki ML, Jones JM. Hydrothermal processing of microalgae using alkali and organic acids. Fuel 2010;89(9):2234–43.
[20] Rushdi AI, Simonet RR. Condensation reactions and formation of amides, esters, and nitriles under hydrothermal conditions. Astrobiology 2004;4(2):211–24.
[21] Schouw NL, Danteravanich S, Moshka H, Tjell JC. Composition of human excreta—a case study from Southern Thailand. Sci Total Environ 2002;286(1–3):155–66.
[22] Schouw NL, Danteravanich S, Moshka H, Tjell JC. Composition of human excreta—a case study from Southern Thailand. Sci Total Environ 2002;286(1–3):155–66.
[23] Schouw NL, Danteravanich S, Moshka H, Tjell JC. Composition of human excreta—a case study from Southern Thailand. Sci Total Environ 2002;286(1–3):155–66.
[24] Valdez PJ, Tocco VJ, Savage PE. A general kinetic model for the hydrothermal liquefaction of microalgae. Bioreourc Technol 2014;163:123–7.
[25] Wang W, Xu Y, Wang X, Zhang B, Tian W, Zhang J. Hydrothermal liquefaction of microalgae over Transition metal supported TiO2 catalyst. Bioreourc Technol 2017. http://dx.doi.org/10.1016/j.biortech.2017.11.051.
[26] Wang W, Yu Q, Meng H, Han W, Li J, Zhang J. Catalytic liquefaction of municipal sewage sludge over transition metal catalysts in ethanol-water co-solvent. Bioreourc Technol 2017;249:361–7.
[27] Wang YP, Nan G, Wang WJ, Zhang JL, Han W. Preparation and application of a new catalyst to produce bio-oil from microalgae liquefaction. Int J Agric Biol Eng 2017;10(1):169–75.
[28] Watanabe M, Aizawa Y, Iida T, Nishimura R, Inomata H. Catalytic glucose and fructose conversions with TiO2 and ZrO2 in water at 473 K: relationship between reactivity and acid-base property determined by TPD measurement. Appl Cat A 2005;295(2):150–6.
[29] Watanapaphawong P, Rehuvycharam P, Yamaguchi A. Conversion of cellulose into lactic acid using zirconium oxide catalysts. RSC Adv 2017;7(30):18561–8.
[30] WHO, UNICEF. 2017. Progress on drinking water, sanitation and hygiene. In: Joint Monitoring Programme 2017 update and SDG baselines. https://www.unicef.org/publications/index_96611.html > [checked in Nov,24, 2017].
[31] Xiu SN, Shahbazi A, Shirley V, Cheng D. Hydrothermal pyrolysis of swine manure to bio-oil: effects of operating parameters on products yield and characterization of bio-oil. J Anal Pyrolyl 2010;88(1):73–9.
[32] Xiu SN, Shahbazi A, Wang LJ. Co-liquefaction of swine manure with waste vegetable oil for enhanced bio-oil production. Energy Sources Part A-Renewable Environ Effects 2016;38(4):459–69.
[33] Xue Y, Chen HY, Zhao WN, Yang C, Ma P, Han S. A review on the operating conditions of producing bio-oil from hydrothermal liquefaction of biomass. Int J Energy Res 2016;40(7):865–77.
[34] Yim SC, Quitaín AT, Yusp S, Sasaki M, Uemura Y, Kida T. Metal oxide-catalyzed hydrothermal liquefaction of Malaysian oil palm biomass to bio-oil under supercritical condition. J Supercrit Fluids 2017;120:384–94.
[35] Zhang B, von Keitz M, Valenta K. Thermochemical liquefaction of high diversity grassland perennial. J Anal Pyrolyl 2009;84(1):18–24.
[36] Zhang C, Tang XH, Sheng LL, Yang XY. Enhancing the performance of Co-hydrothermal liquefaction for mixed algae strains by the Maillard reaction. Green Chem 2016;18(8):2542–53.
[37] Zhang JG, Yan N. Formic acid-mediated liquefaction of chitin. Green Chem 2016;18(18):5050–8.
[38] Zhang L, Xu GC, Champagne P, Mabee W. Overview of current biological and thermo-chemical treatment technologies for sustainable sludge management. Waste Manag Res 2014;32(7):586–600.