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Catalytic liquefaction of human feces over Ni-Tm/TiO_2 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/TiO_2 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/TiO_2 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 CO_2, CH_4, and C_2H_6. Hydrothermal liquefaction over Ni-Tm/TiO_2 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 origin of the 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 TiO_2 catalyst greatly improved the HTL of high-protein-content microalgae Spirulina [36]. This study convinced us that rare earth element and nickel supported on TiO_2 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.

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Table 1
Proximate and ultimate analysis of feedstock.

Parameters	Human feces		Sludge [35]	Nannochloropsis [34]
	This study	[18]		
Proximate analysis (%)				
TS (Total solid)	15.13 ± 1.93	19.6 ± 3.8	15.48	–
Ash[a]	9.28 ± 0.42	17.0 ± 1.3	23.01	6.8
Biochemical analysis (%)				
Protein	45.28 ± 1.94	–	37.84	66.5
Lipid	13.50 ± 1.10	–	8.01	23.2
Carbohydrate	31.94 ± 0.89	–	31.14	10.3
Organic element analysis (%)				
C	50.51 ± 1.06	42.4 ± 1.3	46.68	47.08
H	6.75 ± 0.31	6.9 ± 0.9	6.85	8.77
O[b]	35.76 ± 0.90	43.1 ± 3.1	37.60	34.54
N	6.05 ± 0.49	5.9 ± 1.0	8.05	8.07
S	0.53 ± 0.02	1.7 ± 0.5	0.81	1.54

[a] Based on dry biomass.
[b] Calculated by difference.

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/TiO_2 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 $Tm(NO_3)_3{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, TiO_2 powder, and HNO_3 were all of the pure analytical grades and purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Nitrate neodymium, 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.

2.2. Preparation of bimetallic catalyst

The catalyst preparation was based on our previous research [36]. Wet impregnation method was applied to prepare the catalyst precursor. TiO_2 and the amounts of $Tm(NO_3)_3{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ needed stoichiometrically for catalyst contain 10 wt% Ni and 10 wt % Tm. The TiO_2 was acidized by 1.0 mol/L nitric acid for 4 h, washed with deionized water and then dried at 105 °C for 8 h. The nickel and thulium precursors were dissolved in water and mixture together, and deionized water was added to the solution to bring the total volume to 2.5 mL of liquid per gram of dry TiO_2. The solution was slowly dispensed onto the TiO_2 support with continuous stir for 12 h. The impregnation liquid was separated from well-impregnated catalyst precursor by decantation. The wet catalyst precursor was dried at 105 °C for 24 h and then was calcinated in a muffle furnace at 700 °C for 4 h. The obtained catalyst was labeled as Ni-Tm/TiO_2. XRF analysis determined that the obtained Ni-Tm/TiO_2 catalysts consist of with 5.28% of NiO, 4.47% of Tm_2O_3 and 90.25% of TiO_2. The catalysts of Ni-Nd/TiO_2, Ni-La/TiO_2, and Ni-Ce/TiO_2 were prepared with the same method.

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.

$$\text{Biocrude yield} \quad (Y_B,\%) = \frac{M_B}{M_{F(daf)}} \times 100 \tag{1}$$

$$\text{Gaseous product yield} \quad (Y_G,\%) = \frac{M_G}{M_{F(daf)}} \times 100 \tag{2}$$