Fuel 232 (2018) 141–146

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

# Thermal characterization and pyrolysis of digestate for phenol production

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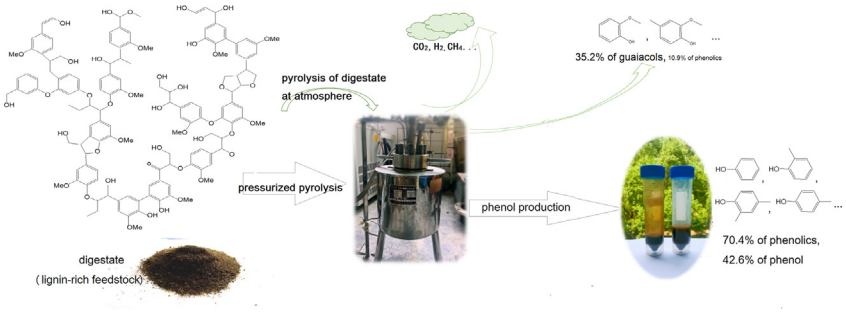
## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Keywords:*
Digestate
Pyrolysis
Bio-oil
Phenol

## ABSTRACT

Digestate, the residue following of anaerobic digestion, had attracted great attention recently as potential feedstock of pyrolysis. The results of component analysis verified that digestate was suitable for phenol production due to its considerable lignin content. The thermal degradation of lignin in digestate mainly occurred around 350–450 °C in thermogravimetric analysis. The amorphous cellulose in digestate decomposed to short-chain acids, water and syngas rather than furfural at low temperature around 280 °C. Pyrolysis of digestate for phenol production was conducted under different reaction temperature and pressure. High reaction temperature contributed to phenol formation by facilitating the cleavage reactions of β-O-4 and C–C linkages among three phenylpropane units in lignin. Pyrolysis pressure promoted secondary monomolecular dissociation reactions of methoxyphenol to yield phenol and alkyl-phenol. The maximum phenolics (70.4%) and phenol (42.6%) contents were achieved at 450 °C with 5 MPa pressure in this work.

## 1. Introduction

The conversion of biomass to energy sources such as biogas and biofuel currently has drew great attention, since the limitation on storage of fossil fuels as our primary energy source [1,2]. Anaerobic digestion is a well-developed technology owing several advantages over other technologies on bio-fuel production, for waste treatment, its mild reaction condition and considerable yield of gaseous products [3,4]. Nevertheless, the development of anaerobic digestion has been found in a tight corner, because of the digestate byproduct during the fermentation process. Digestate, the residue following anaerobic digestion of feedstock, mainly consists of not biodegradable feedstock and pathogen [5]. Currently, the digestate is widely used as fertilizer and fish feed, which, however, cannot meet the requirement for industrial scale treatment. In addition, there is a concern about spreading the heavy metals and pathogen content in the digestate if not controlled properly [6].

Researchers have put huge efforts on alternative uses of digestate in

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https://doi.org/10.1016/j.fuel.2018.05.134
Received 12 March 2018; Received in revised form 3 May 2018; Accepted 27 May 2018

recent years. Pyrolysis is regarded as a technology with great potential to treat the wastes. Related studies have found over 91% of the digestate energy was transferred into products of bio-oil, solid and gaseous [5]. Nowadays, scientists have concentrated on its solid product [7], which shows good soil amendments properties [8]. However, the accumulation of ash in digestate sets up a barrier to improving the quality of biochar product [9,10]. Bio-oil production opens a new horizon toward digestate utilization, because the processes not only minimize the limitation caused by ash, but also prevent ash appearing in the desired product. Digestate pyrolysis oil shows promise as a biofuel source for engine applications [11]. However, related studies on component of pyrolysis oil are still lacking.

To achieve a better understanding of digestate pyrolysis, it is important to clarify the composition and properties of the feedstock. During anaerobic digestion, the vast majority of cellulose and hemicellulose takes decomposition accompany with methane generation. Nonetheless, lignin has not been used during the process and is regarded as the main constituent of digestate [12]. Relevant researchers have treated lignin as favorable feedstock for phenol production, because it mainly consists of three phenylpropenyl units: coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [13]. Catalytic pyrolysis on lignin represented remarkable yield (66.9%) of phenolics in the obtained bio-oil [14]. Nevertheless, tremendous literature studies on lignin pyrolysis mainly base on the purified lignin feedstock derived or extracted via specific methods, while only limited studies have been conducted on residues, especially the digestate [15].

With the intention to further determine the concept of digestate decomposition and phenol production, digestate was applied on pyrolysis to produce phenol rich bio-oil in this study. The digestate was obtained from anaerobic digestion in laboratory. The composition analysis and thermogravimetric analysis were conducted. Experiments had been taken on investigating the impact of the reaction temperature and pressure on digestate pyrolysis, as well as characterizing the yield and quality of bio-oil product. Further objectives were to propose the optimum reaction from digestate to phenol, and find a feasible foundation of digestate decomposition mechanism for further utilization.

## 2. Methods

### 2.1. Materials

Cellulose (CAS 9004-34-6) was purchased from Aladdin (Aladdin Bio-Chem Technology Co., LTD in Shanghai, China).

Chloroform (CAS 67-66-3, 99.0 wt%) was purchased from Aladdin (Aladdin Bio-Chem Technology Co., LTD in Shanghai, China).

Digestate using sargassum horueri as fermentation feedstock was obtained from mesophilic lab-scale biogas production in the laboratory. Sargassum horueri, suitable for biogas fermentation, purchased from Wenzhou, Zhejiang province, China. The digestate was oven-dried at 105 °C for 24 h, crushed by grinder and sieved into 20-mesh particle before use.

### 2.2. Characterization of digestate

Cellulose, hemicellulose and lignin contents of the digestate were determined as follows [16]: the digestate was boiled with 5 mL of 72 wt % $H_2SO_4$ solution for 4.5 h to hydrolyse the cellulose and hemicellulose. The suspension remaining dried at 105 °C for 24 h and weighted, then the residue heated at 600 °C for 5 h and weighted for lignin determination. The glucose and reducing sugar contents in filtrate from $H_2SO_4$ treatment were measured via HPLC and DNS method [17]. Then the cellulose and hemicellulose contents were calculated according to the contents of glucose and reducing sugar.

Moisture content in feedstock was determined gravimetrically in oven at 110 °C according to ASTM D2216-98. Ash content was measured base on ASTM E1534-93, in which sample was heated in a muffle furnace at 600 °C, further repeat the heating for 30 min periods until the weight is constant. The volatile matter determination according to ASTM D3175-11 was carried by making sample heating in a muffle furnace at 950 ± 20 °C for 7 min. Elements such as C, H, N, S were determined by elementary analyzer “Elementar Vario Macro”. Proteins content was estimated by multiplying total nitrogen content (N) by 6.25.

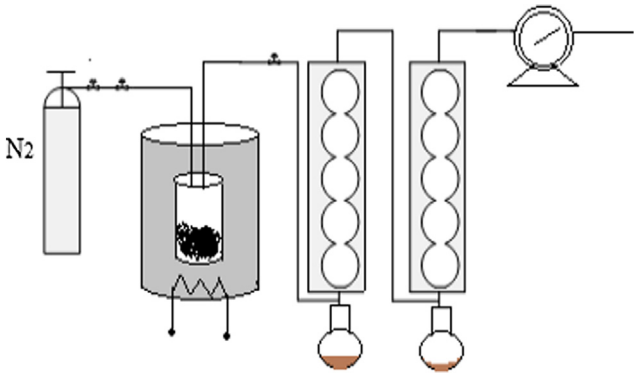


**Fig. 1.** Schematic diagram of experimental system.

Thermogravimetric analyser (TG209F3, Netzsch, Germany) was used to illustrate the thermal-dynamic properties of digestate. Approximately 10 mg of samples were progressively heated from room temperature to 800 °C, under a heating rate of 5 °C/min and a constant Nitrogen flow.

### 2.3. Experimental procedure

The digestate sample (about 30 g) has been subjected to the process of pyrolysis in a stainless steel reactor (Fig. 1). Ethylene glycol in water solution was used as the condensate at -5 °C. Prior to each experimental trial, the reactor was purged with $N_2$ for 20 min to ensure oxygen free. The pyrolysis heating rate was employed at 5 °C/min to specific temperature. The pressure within the reactor was regulated by a valve at the outlet of the reactor. Digestate within the reactor was held at specified temperature and pressure for 20 min, and then the volatiles was released. The heavier volatiles were condensed as bio-oils and the rest were treated as syngas and measured by wet-gas flowmeter. The char left in the reactor was collected and weighted.

The bio-oil obtained in this work could be separated into two phases, the oil-phase and the water-phase. Prior research had mentioned the organics in water-phase contained 52.25 wt% of phenol and guaiacols, thus the bio-oil extraction had also been applied on our project following the procedures listed in Wei et al. [18] work. The organics extracted was distilled to remove the solvent, then mixed with oil phase for further analysis.

### 2.4. Characterization of bio-oil product

The chemical composition of bio-oil was determined with an Agilent gas chromatography–mass spectrometer (GC–MS; GC, Agilent 7890A; MS, Agilent 5975C) with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). The GC was programmed to heat to 50 °C for 6 min followed by heating to 200 °C at a rate of 3 °C/min and maintained for 2 min. Afterwards, heating to 280 °C at a rate of 5 °C/min and maintained for 2 min. A high-purity helium stream as the carrier gas. The flow rate of the carrier gas (helium) was 1.0 mL/min. Compounds were identified by comparing the spectral data with that in the NIST Mass Spectral library [19,20]. Besides, the moisture content in bio-oils was tested by the Karl Fischer titrator (Metrohm 870 KF Titrino plus) accordance with ASTM E203-08.