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# Coupling hydrothermal liquefaction and membrane distillation to treat anaerobic digestate from food and dairy farm waste

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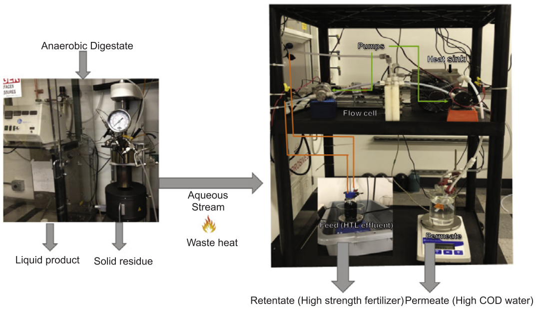
## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Increased demand for water, energy and food requires new ways to produce fertilizers, fuels and reusable water. Recovery of resources from wastes could lead to an additional source of energy and nutrients, and also reduce the waste to be disposed. In this work, we used hydrothermal liquefaction to produce a biocrude oil product, followed by membrane distillation of the aqueous effluents to concentrate a nutrient-rich stream that can be used as fertilizer. The motivation for this work is that residual heat from the hydrothermal liquefaction process could be utilized to drive the membrane distillation process, which would improve the efficiency and reduce the cost of the distillation process. The membrane distillation system was demonstrated to be able to recover 75% of the water. The membrane distillation retentate had very high ammonium and phosphate concentrations, making it suitable as a fertilizer. Membrane permeate contained high concentrations of volatile organics.

## 1. Introduction

Fertilizers have played a critical role in the development of agriculture by substantially improving crop yields, and their importance is growing as the population increases. Commercial fertilizers are composed primarily of nitrogen, phosphorous and potassium, with several also containing some organic species (Romero et al., 2013). Fertilizer production is an energy intensive process, accounting for approximately a third of the energy consumption during US crop production (Gellings and Parmenter, 2016). The main source of

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phosphorous is phosphate rock, which is mined in several locations around the globe (primarily in Morocco, China and South Africa (Van Kauwenbergh, 2010)). During the fertilizer manufacturing process, phosphate rock is converted to various forms of soluble orthophosphates (Rehm, 1997). However, natural phosphate rock deposits are dwindling, which could have dramatic impacts on global agricultural yields (Gilbert, 2009). Nitrogen in fertilizers is generated through the Haber-Bosch process, where atmospheric nitrogen is converted to ammonia in a process that requires hydrogen which is usually generated from steam reforming of methane (Sutton et al., 2011). Given the high energy costs, and dwindling precursor materials, an attractive alternative to current fertilizer production methods is the recovery of nitrogen and phosphorous species from various waste streams (Ren and Umble, 2016). Various resource-recovery methods have been explored, with many investigations reporting the extraction and recovery of nitrogen and phosphorous from waste such as municipal and industrial wastewater, manure lagoons, and landfill leachate (Abdel-Raouf et al., 2012; Xie et al., 2014).

Due to its high reliance on dairy as a food source, the United States has a large number of dairy farms; a 2014 USDA report states that there were over 9.2 million milking cows, with this number growing steadily (James and Macdonald, 2014). Each cow produces 20–30 tons of liquid manure every year, which translates into the production of 180–200 million cubic meters of manure per year. Liquid manure is rich in organic carbon, and nutrients such as nitrogen, phosphorous and potassium (Eghball and Power, 1999). A common treatment strategy for this waste is anaerobic digestion, which converts approximately 50% of the biomass into biogas that is used as a source of heat and electricity (De Meester et al., 2012). Liquid effluent from anaerobic digestion (known as digestate) contains large amounts of organics and nutrients. Traditionally, anaerobic digestate is disposed of in landfills or sent to a wastewater treatment plant (Arnon et al., 2008; Inoue et al., 2002). In addition to wasting valuable resources, this practice can result in soil and groundwater pollution, due to leaching (Hombach et al., 2003). Digestate may also be directly applied to agricultural land as fertilizer. Direct spreading of digestate on land is not recommended during winter, however, as excess precipitation can cause it to run off the land and contaminate local water sources. This need for seasonal application results in large storage requirements (Tambone et al., 2010). Further, since dairies tend to be clustered, this leads to the clustering of biogas plants and the oversupply of digestate in certain regions (Al Seadi et al., 2013). Thus, the digestate either needs to be transported to remote agricultural land that is nutrient deficient, or processed in a different way. Since digestate is 95% water, the transportation of this liquid product is economically and logistically complicated. Many biogas plants separate the solid and liquid fractions of digestate and then use the solid fraction as fertilizer, with the liquid fraction requiring further treatment (Al Seadi et al., 2013). This practice leaves two concentrated streams containing organic carbon and nutrients. However, crops do not require such large amounts of organic carbon to be provided through soil. Thus, a better utilization of the carbonaceous fraction found in digestate would be to valorize this carbon into a useful form of fuel, and in addition, recover the nutrients in a concentrated form that can be readily transported. One way to achieve both these goals along with producing a stream of treatable water is by the integration of two energy efficient processes; hydrothermal liquefaction (HTL) and membrane distillation (MD). A brief description of both these processes follows.

HTL is an attractive technology for the production of energy products and bio-based chemicals from high-water-content biomass (Angenent et al., 2017). The main advantage of HTL is the use of water as the reaction media. This is in contrast to conventional dry thermochemical processes (i.e., pyrolysis or gasification) where water has to be removed prior to the process (Peterson et al., 2008). Therefore, HTL offers opportunities for valorization of wet-waste streams, such as food waste and manure (Yin et al., 2010). HTL typically takes place over a range of temperature (280–380 °C), pressure (7–30 MPa) and reaction time (10–60 min) conditions (Peterson et al., 2008). These conditions allow the production of bio-crude oil (liquid) and hydro-char (solid) products along with some biogas, all with higher heating values than the raw feedstock (Biller et al., 2013). HTL has been tested with a variety of biomass feedstocks, particularly in regard to the bio-crude oil and hydro-char products (Biller et al., 2015; Posmaniket al., 2017a; Qian et al., 2017). In addition, the HTL process also produces a significant amount of an aqueous-phase product, traditionally considered a waste. One possibility of valorizing the HTL aqueous effluents is by considering it as a secondary feedstock for bioenergy production via anaerobic digestion and gasification processes (Elliott et al., 2015; Posmaniket al., 2017b; Van Doren et al., 2017). Since the HTL aqueous effluents have resulted from a thermochemical process, they are sterile and hot, and therefore may be a feasible feed for MD processes. In this configuration, the residual heat present in the HTL aqueous effluent is used to drive the MD process, which uses thermal energy to separate volatiles (water, volatile organics) from non-volatiles (nutrients) (Alkhudhiri et al., 2012).

MD is a membrane-based water treatment method that uses a vapor-pressure gradient across a hydrophobic membrane as the driving force for the transport of water vapor (and other volatiles) across the membrane, while preventing liquid water (which contains the contaminants) from passing through the membrane (Alkhudhiri et al., 2012; Lawson and Lloyd, 1996). In MD, the vapor-pressure gradient is induced by a temperature gradient between the feed stream and the permeate stream, which are separated by the membrane itself. Because the process blocks liquid water from passing through the membrane, and because the driving force is not a pressure differential, MD is typically used for treating highly contaminated waste streams with low concentrations of volatile species (Curcio and Drioli, 2005). Membrane distillation faces several challenges such as membrane fouling, wetting, high energy requirements and the inability to separate volatile compounds (Curcio and Drioli, 2005). Fouling occurs when organic and inorganic materials in the feed deposit on the membrane surface, partially or completely blocking the passage of water vapor, which causes a decrease in the permeate flux (Dudchenko et al., 2014). Because MD relies on the prevention of liquid water from passing through the membrane, it is essential that the membrane is not wetted (i.e., allow the passage of liquid water through the pores) (García-Payo et al., 2000). Thus, operating conditions in the MD module have to be maintained such that transmembrane pressure does not exceed the liquid-entry pressure, defined as the minimum transmembrane pressure causing the water in the feed to enter the membrane pores (Goh et al., 2013). However, membrane wetting can also occur as a result of the deposition and accumulation of organic and inorganic species within the membrane's pores (Franken et al., 1987). For example, amphiphilic organic molecules can sorb onto the hydrophobic pores of the membranes, which creates a hydrophilic surface that can be readily accessed by contaminated liquid water (Franken et al., 1987). Once the membrane is wetted and contaminated liquid water passes into the permeate, the performance of the membrane rapidly plummets (Goh et al., 2013). Since the MD process relies on a thermal driving force, the process is considered highly energy intensive due to water's high heat capacity (Lawson and Lloyd, 1996). Thus, for MD to be economically feasible, it needs to be applied to either high-salinity brines or a waste (i.e., free) heat source needs to be available (Alkhudhiri et al., 2012).

Here, we report on the performance of an integrated energy-efficient process, which aims to convert the organic carbon contained in anaerobic digestate into bio-crude oil, while concentrating nutrients to produce a high-strength fertilizer and generating a stream of water that can be readily disposed. The integrated approach described in this paper is based on a two-step process, where first the digestate is processed using hydrothermal liquefaction (HTL) to produce valuable hydrocarbons (energy), and then the aqueous effluent from the HTL process is treated using membrane distillation (MD) produce two