



## Case report

# Bio-methane from an-aerobic digestion using activated carbon adsorption



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## ABSTRACT

There is an increasing global demand for carbon-neutral bio-methane from an-aerobic digestion (AD) to be injected into national gas grids. Bio-gas, a methane-rich energy gas, is produced by microbial decomposition of organic matter through an-aerobic conditions where the presence of carbon dioxide and hydrogen sulphide affects its performance. Although the microbiological process in the AD can be tailored to enhance the bio-gas composition, physical treatment is needed to convert the bio-gas into bio-methane. Water washing is the most common method for upgrading bio-gas for bio-methane production, but its large use of water is challenging towards industrial scale-up. Hence, the present study focuses on scale-up comparison of water washing with activated-carbon adsorption using HYSYS and Aspen Process Economic Analyzer. The models show that for plants processing less than 500 m<sup>3</sup>/h water scrubbing was cost effective compared with activated carbon. However, against current fossil natural-gas cost of about 1 p/kWh in the UK both relied heavily on governmental subsidies to become economically feasible. For plants operating at 1000 m<sup>3</sup>/hr, the treatment costs were reduced to below 1.5 p/kWh for water scrubbing and 0.9 p/kWh for activated carbon where the main benefits of activated carbon were lower capital and operating costs and virtually no water losses. It is envisioned that this method can significantly aid the production of sustainable bio-methane.

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## 1. Introduction

Biogas produced by an-aerobic digestion of agricultural manure wastes, sewage sludge and food wastes has the potential to replace up to 50% of the UK's 2014 natural gas need of about 850 TWh [1]. However, there were only 157 biogas plants in 2014 generating a total of 0.71 TWh/year mostly through combined heat and power (CHP) production [2]. Although an-aerobic digestion is the most common commercial bio-gas production process, there are several aspects on the interface between the microbiological science and the practical technology application that still need to be optimised for bio-gas to be turned into bio-methane for gas grid injection [3]. The production of methane-rich bio-gas involves the collective activity of various microorganisms with varied metabolic growth needs [4–7]. Microbial dynamics are intensely associated with a

range of operational factors, such as temperature of the process, loading rate, and retention time [8–11]. To ensure a steady and effective bio-gas production process, a balanced combination of micro and macronutrients is normally added to the digester [12,13]. In addition, ammonia and dihydrogen sulphide generation can be suppressed by the use of trace metals, iron or buffering chemicals. The chemical configuration affects the yield of biogas and, accordingly, the methane concentration of the gas but can also affect the techno-economic performance of the AD [14–16]. Bio-gas can be produced at varying temperature conditions, specifically mesophilic (35–42 °C), thermophilic (45–60 °C) or psychrophilic temperature (16–25 °C). Substrate with temperature impact strongly on the structure of the community and microbial diversity as these parameters best describe the consistency and performance of the process [7,17]. Usually, higher methane production is achieved at thermophilic temperature, but this is not always the case [18,19]. Moreover, high temperature requires more energy input resulting in lower microbial diversity and also resulting in higher operating costs [18]. Methanogenic community has been shown to shift from hydrogenotrophic methanobacterales towards

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hydrogenotrophic methanospirillum and strict acetoclastic methanosaeta representatives with decreasing of retention time and an increasing loading rate [6,20]. However, high concentration of volatile fatty acids (VFA) may accumulate during sludge digestion in AD configuration operated at high organic loading rate (OLR) or shortened hydraulic retention time (HRT) [7]. The direct effect of increasing loading rate is usually enhanced overall activity of primary fermenting bacteria with increased VFA production [21]. Under non-stress conditions, it was observed that at high HRT of more than 50 days Clostridiales was the main active bacteria, while at shorter HRT of 30–40 days, the phylum Bacteroidetes dominate the bacterial consortia along with the Clostridiales. For HRT of 15 days the Bacteroidetes were found in great numbers while for extreme short HRT of 2 days, the Firmicutes were the exclusive dominant phylum [22]. This shows that bacteria cultures can be selected that optimise the HRT and temperature used for later processing [23–25].

For this reason, in the current research, three different process temperatures of 25, 50 and 75 °C were selected for conversion of bio-gas into bio-methane. However, the main barrier for increased biogas upgrading into bio methane, is the removal of hydrogen sulphide and carbon dioxide [6,26,27]. Gas-to-grid cleaning and injection technologies are expensive, but cost can be decreased with increasing scale [28]. In the UK, all gas converted into a gas transporter pipeline must comply with the quality requirements set out in the gas safety management regulations, described in Table 1 [29]. Hence, clean-up of bio-gas to allow injection of bio-methane into the gas network requires investment in appropriate plant and its operation and to mitigate these costs some UK government support systems are available for bio-methane injection to grid [30].

Various bio-gas upgrading methods, including activated carbon adsorption (AC), water scrubbing (WS), pressure swing adsorption (PSA), membrane separation (MS) and cryogenic separation (CS) have been industrial applied [31–33]. Each method has advantage and disadvantages, and, in this article, the water scrubbing method is compared with the activated carbon for the economic viability of the upgradation process. Generally, water washing has higher operational costs and requires more energy compared to activated carbon that has numerous benefits as it is very efficient, economical and low energy regeneration, but requires regeneration [34]. The activated carbon adsorption compared with the water scrubbing method as currently, this is the most commonly used method for production of bio-methane [6,35].

The main issue associated with water scrubbing is the high operating costs [36]. The reported costs of bio-gas upgrading for methane production with water washing were 2.7p/kWh for 250 m<sup>3</sup>/hr plant capacity and 1.94p/kWh and 1.45p/kWh for 500 m<sup>3</sup>/hr and 1000 m<sup>3</sup>/hr plant size respectively, which shows that the cost of the bio-gas upgradation decrease with the increase in the plant capacity [37,38]. To compensate for this various governments have put in place incentives to stimulate bio-methane generation, where the UK government has used the RHI [39]. The uniqueness of the activated carbons as adsorbent is their high surface area, developed pore volume and surface properties [40]. Activated carbon which is highly porous materials used for removal of impurities from the liquids and gases including purification, gas separation and environmental technology [41]. Among the various methods used to clean-up the bio-gas, physical adsorption by activated carbon bed is the most attractive and convenient desulphurization method [42]. Although the strong adsorption has traditionally hindered the desorption process, there have been evidence that AC can be regenerated in-situ at a rate similar to adsorption [43].

Hence, this work compares the design of the water scrubbing

and activated carbon processes for the upgrading of medium sized AD system up to 1000 Nm<sup>3</sup>/hr of bio-gas. For this purpose, a 60 cm<sup>3</sup> activated carbon column was commissioned. A gas mixture consisting of 40% carbon dioxide, 60% nitrogen and 1% hydrogen sulphide was used to simulate biogas. Different samples of activated carbon were tested for CO<sub>2</sub> and H<sub>2</sub>S adsorption capacities at different temperatures. Accordingly, scale-up comparison and economic viability of water washing with activated-carbon adsorption was carried out using HYSYS and Aspen Process Economic Analyzer (APEA). It was concluded that the use of activated carbon for bio-gas upgrading reduced the annual operating costs by 64.5% and the capital costs by 17.3% compared to water scrubbing. Thus, combined with microbial advancements, bio-methane could play an important role in the future as a secure, affordable and sustainable energy source.

## 2. Experimental

### 2.1. Activated carbon

Three different commercial activated carbon samples were used in the adsorption study and referred as AC-1, AC-2 and AC-3, respectively. Each sample of activated carbon was chosen with different physical structure. AC-1 is small grains physical appearance, AC-2 in pallet form whereas AC-3 is in powder form. These activated carbons were selected with respect to good adsorption properties for the removal of hydrogen sulphide.

Elemental analyses of carbon, hydrogen and nitrogen (C, H, and N) were conducted using a 440 Elemental Analyzer (Control Equipment Cooperation) with helium as carrier gas. The standard ASTM method was used to determine the total ash content by heating the activated carbon samples at 750 °C with heating rate of 100 °C/min for 8 h.

Nitrogen isotherms were measured using a Micrometrics Gemini VII. The activated carbons were degassed for 12 h at 200 °C under nitrogen using Micrometrics Flow prep 060. The specific surface area, micro-pore volume, total pore volume and pore size distributions were calculated using the Density Functional Theory (DFT) [44]. The surface area was calculated using the BET method. Table 2 shows the properties of the activated carbon samples.

TGA analyses were conducted in the TA analyzer (Normal-Q500 TGA). About 23 mg of AC was used for the recycled adsorption and desorption at different temperatures. Initially, temperature in the TGA was raised up to 100 °C for 20 min to remove of any moisture content present in the sample using only nitrogen. Then temperature was set to 25 °C for about 4 h to investigate the repeated adsorption and desorption curves. The temperature was then increased from 25 to 50 °C for next 3.5 h to observe the adsorption and desorption of the carbon dioxide. The temperature was further raised to 75 °C to evaluate the adsorption desorption analyses.

### 2.2. Process setup

A schematic diagram of the adsorption process is shown in Fig. 1. The apparatus consist of stainless steel column (21.5 mm I/D, 290 mm length) with the glass wool and filter paper placed to avoid the slippage and proper packing of activated carbon samples inside the bed. Nitrogen, carbon dioxide and hydrogen sulphide gas mixtures were used and volume flow meters (FLDN3505, Omega Engineering Limited) were mounted to calculate the gas flow rates. Nitrogen used as carrier gas whereas the carbon dioxide and hydrogen sulphide used for adsorption/desorption analysis. Mass-spectrometer (Hidden Analytical Ltd.) was used to measure the mass of gases. Nitrogen and carbon dioxide supplies from the laboratory where a special gas cylinder was procured with 99%

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