

# PRODUCTION OF BIOMETHANE FROM AGRICULTURAL WASTE USING A CRYOGENIC CARBON CAPTURE PROCESS

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## ABSTRACT

This paper evaluates a novel cryogenic carbon capture process to upgrade biogas produced from agricultural waste. The A3C cryogenic process offers simplicity and compactness with lower capital and operating costs compared to many alternative processes. The work addresses potential technical issues presented by trace contaminants in the raw biogas including hydrogen sulphide, organics and siloxanes. It is found that the A3C process offers high CO<sub>2</sub> removal with minimal biomethane losses while requiring simple raw gas treatment.

**Keywords:** agricultural waste, anaerobic digestion, cryogenic carbon capture, anti-sublimation

## NONMENCLATURE

### Abbreviations

A3C	advanced cryogenic carbon capture
AD	anaerobic digestion
CHP	combined heat and power
GHG	greenhouse gas emissions
GWP	global warming potential
Th <sub>MP</sub>	theoretical biomethane potential
VS	volatile solids

### Symbols

MtCO <sub>2e</sub>	million tonnes of CO <sub>2</sub> equivalent
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## 1. INTRODUCTION

The European Union (EU) 2050 commitment to reduce GHG emissions by 80-95% compared to 1990 levels is driving the quest for solutions with near-zero emissions [1]. For the UK, 42 MtCO<sub>2e</sub> came from the

agricultural sector in 2016; these contribute to 10% of the total UK GHG emissions, which include methane (62%) due to enteric fermentation from cattle, nitrous oxide (35%) due to fertilisers used on soils, and CO<sub>2</sub> (3%) [2]. GHG emissions reduction has focused more recently on CO<sub>2</sub> emissions; however, methane poses a higher global warming potential (GWP) of 84 for a lifetime of 20 years and 28 for 100 years relative to CO<sub>2</sub> [3], since CH<sub>4</sub> has a higher radiative energy impact but over a shorter atmospheric lifetime than CO<sub>2</sub>.

Anaerobic digestion (AD) is used to produce biogas from various sources. The biogas typically consists of 53–70% of CH<sub>4</sub>, 30–47% of CO<sub>2</sub> and other impurities, and can be used for electricity and heat generation [4]. Biogas is then a renewable energy source that can replace gas derived from fossil fuels.

Upgrading biogas to higher methane content, often called biomethane, is growing interest due to support schemes for applications as a vehicle fuel and for injection into the natural gas grid in Europe –world's leading producer of biomethane [5]. There are 17,358 biogas plants in Europe with a total installed capacity of 8.7 GW<sub>e</sub> in 2015, and 367 biomethane AD plants with a total upgrading capacity of 310,000 m<sup>3</sup>/h of raw biogas in 2014. In the UK, 473 AD plants operate using agricultural and waste feedstock. Sixty-two use 723 kt/y of cattle manure, cattle slurry or a mixture with other agriculture waste, mostly for CHP, with capacities ranging from 3 to 1,170 kW<sub>e</sub> [6].

Biomethane usually contains 97–99% CH<sub>4</sub> and 1–3% CO<sub>2</sub>. For pipeline injection, typical specifications require CO<sub>2</sub> content of less than 3%, and as vehicle fuel a combined CO<sub>2</sub>-N<sub>2</sub> content of 1.5–4.5%. The main biogas upgrading technologies and their performance are as follows: i) water scrubbing, >97% CH<sub>4</sub> and

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simultaneous hydrogen sulphide (H<sub>2</sub>S) removal, ii) chemical absorption/scrubbing, >99% CH<sub>4</sub> with very low CH<sub>4</sub> losses (<0.1%), iii) pressure swing adsorption, 95–98% CH<sub>4</sub>, and iv) membranes, >96% CH<sub>4</sub> [7]. Alternatively, cryogenic/low-temperature upgrading technologies can be used to deliver 90–98% CH<sub>4</sub>, with CO<sub>2</sub> in high purity, where the purified gas can be obtained directly at low temperatures to readily produce liquid biomethane (LBM) [4]. The challenge for biogas upgrading technologies is the reduction of their energy intensity to make biomethane more attractive to substitute fossil fuels for heating and transportation.

Cryogenic upgrading often involves multiple beds and heavy frost deposition. Therefore, this paper presents a novel advanced cryogenic carbon capture (A3C) technology that overcomes some limitations of previous cryogenic systems by using a moving bed of metallic beads as a heat transfer medium and frost capture surface. Prior work detailed in [8] modelled the performance and estimated costs of a 720 Nm<sup>3</sup>/h biogas application of the A3C process using Aspen Plus<sup>®</sup>. The work assumed that the biogas consisted of the two major gases methane and carbon dioxide at 65% and 35% vol., respectively. However, the analysis did not consider the potential impacts of trace contaminants in the raw gas. The estimated capital, energy and other operating costs were discounted at 10% over a life of 15 years to calculate a levelised cost of carbon capture. The results for the A3C process were compared with a similar analysis for an MEA amine process in the same application. The significant finding was that the levelised cost for carbon capture by the A3C process was 70% less than that for the amine process.

Since biogas from anaerobic degradation contains other minor compounds, such as H<sub>2</sub>S, oxygen, nitrogen, and hydrocarbons [9], this paper explores the measures necessary to upgrade biogas using the A3C process taking account of the trace contaminants present in biogas derived from agricultural sources.

## 2. METHODOLOGY

### 2.1 A3C process description

The A3C process consists of two stages: a cooling and drying step, followed by CO<sub>2</sub> separation by the desublimation as in figure 1. The raw gases (1) are first pre-treated as necessary to remove trace compounds not separated by the process, and then cooled to 274K conventionally to condense most of the water vapour. The gas (2) enters cooler-drier section in counterflow of a circulating packed bed of small metallic beads (at

about 185K) and cools to about 190K, reducing the water content below 50 ppb. The ice bearing bed material is carried out of the raw gas stream, warmed with low grade heat in a slip steam of raw gas to re-evaporate the water to be recycled and recovered in the inlet chiller.

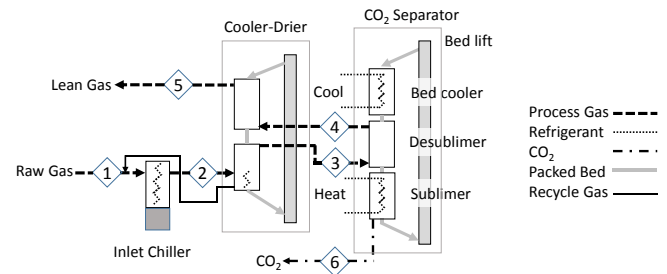
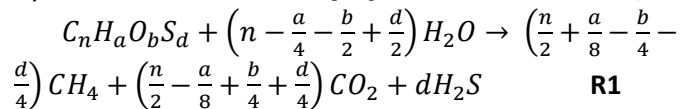


Fig 1 Outline of the A3C separation process

The cold dry gas (3) is passed into the separator, a second circulating packed bed cascade of similar design to the cooler-drier. Here it flows counter to a colder bed, so that the CO<sub>2</sub> in the gas stream deposits as a frost on the bed material. The lowest gas temperature is chosen to correspond to the CO<sub>2</sub> saturation temperature at the desired residual CO<sub>2</sub> content. The bed carries the CO<sub>2</sub> frost into a submerged tube heat exchanger where it is warmed to 195K to recover the CO<sub>2</sub> by sublimation. The bed is then recirculated through a further heat exchanger for cooling to the desired inlet temperature. More details on the A3C process can be found in [8].

### 2.2 Methane calculations

This work studies the upgrading of biogas, and in order to evaluate some potential agricultural sources, some quick estimations were derived. For example, the composition of major biogas products can be estimated by the Bushwell's formula [10] shown as reaction R1,



The theoretical methane yield (L CH<sub>4</sub>/kg VS) can be estimated using Bushwell's formula [10],

$$B_u = \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right) \frac{22.4}{(12n+a+16b)} \quad \text{Eq. 1}$$

## 3. RESULTS AND DISCUSSION

### 3.1 Methane potential

The UK utilises 72% of the land for agricultural use, crops and livestock. Ten million cattle and calves are grown annually, producing large amounts of manure as slurry or solids. This waste could be converted to biogas

by AD. However, it has been reported that co-processing of cattle manure with lignocellulosic biomass is favoured to counter the low and imbalance C/N ratio in animal manures [6]. The UK is a large producer of crops; of the 14.8 Mt produced, 6.4% of the wheat consumed is left for other uses and as waste [11].

Based on the chemical formula for cattle manure and swine solids, table 1 shows the maximum methane composition after AD using reaction R1, and the theoretical methane yield. These values agree with those reported for agricultural waste [9].

Table 1 Theoretical biogas composition and methane yield

Biogas composition (% mol)	Feedlot manure	Swine solids
	CH <sub>1.414</sub> O <sub>0.512</sub> N <sub>0.018</sub> S <sub>0.002</sub> [12]	CH <sub>1.497</sub> O <sub>0.319</sub> N <sub>0.083</sub> S <sub>0.007</sub> [12]
CH <sub>4</sub>	54.4	60.1
CO <sub>2</sub>	44.8	39.1
H <sub>2</sub> S	0.8	0.8
<i>B<sub>u</sub></i> (L CH <sub>4</sub> /kg VS)	0.569	0.732

### 3.2 Requirements for A3C process

#### 3.2.1 A3C process performance

Two plant capacities were evaluated, 720 Nm<sup>3</sup>/h as in [8] for food waste, and 400 Nm<sup>3</sup>/h as a more typical size for agricultural applications. Table 3 shows the raw gas composition used to represent agricultural derived biogas [9], which lies within the values of table 1 in a wet basis, the stream before cooler/dryer, and the biomethane and CO<sub>2</sub> purity. The gas composition for both plant sizes are the same as in table 2, and only the flow rates change. Trace contaminants such as H<sub>2</sub>S remain in the gas phase, whilst benzene and siloxanes are reduced to a minimal level in the pre-cooling stage.

Table 2 Gas composition in % mol.

Stream	1 - Raw gas	2	5	6
CH <sub>4</sub>	58	58.53	94.18	-
CO <sub>2</sub>	38	38.34	1.83	99.99
N <sub>2</sub>	1.5	1.51	2.43	-
O <sub>2</sub>	1	1.01	1.62	-
H <sub>2</sub> O	1.48	0.60	-	-
H <sub>2</sub> S	0.0169	0.0166	0.0268	-
Benzene	2.14x10 <sup>-4</sup>	1.59x10 <sup>-4</sup>	6.17x10 <sup>-7</sup>	3.93x10 <sup>-4</sup>
Siloxanes	0.0293	7.68 x10 <sup>-5</sup>	1.39x10 <sup>-11</sup>	1.56x10 <sup>-7</sup>
Temp (K)	308	273	282	297

Table 3 shows that a reduction of 44% on plant size decreases proportionally the duties of cooler/drier,

desublimer, sublimer and refrigerant compressor, and the bed flow in the core process and cooler/drier.

Table 3 A3C process performance for two plant capacities

Plant Capacity (Nm <sup>3</sup> /h)	400	720
<b>Duties (kW)</b>		
Desublimer	48.3	87.0
Sublimer	61.20	110.2
Refrigerant Compressor	42.7	76.8
Cooler/Drier	13.8	24.8
<b>Bed Flow (kg/s)</b>		
Core	4.7	8.5
Cooler/Drier	0.7	1.2

#### 3.2.2 H<sub>2</sub>S removal

The gas characteristics for injection into the UK gas grid set a maximum H<sub>2</sub>S content of 5 mg/m<sup>3</sup> [13]. The raw gas used in this work contains 245 mg/Nm<sup>3</sup>. This level of H<sub>2</sub>S is found to pass unchanged through the A3C process with the biomethane. Therefore, H<sub>2</sub>S will need to be removed before injection. To avoid corrosion of metallic parts and further equipment, this would be best done before CO<sub>2</sub> capture. Common methods include: physical and chemical absorption; in-situ desulphurization with oxygen/air; adsorption with activated carbon; in-situ addition of iron chloride; and membranes [14]. Each technology poses challenges and some are not suitable for biogas upgrading due to an increase in oxygen content. The use of iron provides several benefits. Adsorption with iron oxide/iron hydroxide has high H<sub>2</sub>S removal efficiency (>99%), but with high operation costs.

#### 3.2.3 Water removal

The A3C process includes a chiller that cools down the biogas and condenses water. The moisture content was reduced by 60% using an inlet temperature of 292K and outlet temperature of 273K, from 1.48% to 0.6% mol. Then, the biogas is sent to a further cooler/drying stage before CO<sub>2</sub> removal, where the low temperatures of the process reduces the water content of the biomethane to less than 100 ppb. The trace organics such as benzene are partly removed by the cooler-drier, being recovered in the chiller condensate.

#### 3.2.4 CO<sub>2</sub> removal

Table 3 shows that 97% of CO<sub>2</sub> is removed and that the CO<sub>2</sub> content in the biomethane is lower than 2% mole, which aligns with recommended values. The CO<sub>2</sub> product stream (6) consists of almost pure CO<sub>2</sub> with 13 mg/m<sup>3</sup> of benzene, which could be useful for high purity

applications. Benzene sublimation data found in the literature [15] were used to verify the modelling of gas-solid equilibria in Aspen Plus®.

### 3.2.5 Siloxane removal

Siloxanes include compounds containing Si-O bonds with methyl and other organic groups. Siloxanes are undesirable because their combustion deposits silica which damages gas processing equipment. Typical removal technologies include adsorption, physical and chemical absorption, biological degradation and cryogenic condensation [16]. Since the A3C process operates at low temperature, modelling shows that siloxanes will be captured during the drying/cooling and CO<sub>2</sub> separation steps, as shown in table 3. Siloxanes were represented by decamethylcyclopentasiloxane (D5), which is expected to be predominant, using Aspen Plus properties.

## 4. CONCLUSIONS

This work investigated the fate of trace components in agricultural biogas when upgraded using a novel cryogenic carbon capture process. The A3C process has been shown to be feasible for the supply of biomethane with low CO<sub>2</sub>, water and hydrocarbons content. The upgraded gas contains 93% of methane and only 2% of CO<sub>2</sub>; however, it needs removal of H<sub>2</sub>S to comply with gas specifications, while benzene is below 20 µg/m<sup>3</sup> and siloxanes are almost fully removed. With the minimal interaction with the trace contaminants, it is not anticipated that the heat exchange and moving bed performance of the A3C process will be affected. The simpler overall upgrading process with its low capital and operating costs make it an attractive proposition for agricultural biogas application. Detailed economic analysis for complete A3C process applications to agricultural biogas is ongoing work for a full paper.

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