New Technologies for Sustainable Valorisation of CH_4 and CO_2 from Livestock and Biogas

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Significance and Relevance

Different adsorbents were tested in silico, then the selected ones in a controlled microreactor and in a real stable to design an adsorption-based process for the direct air capture of CO_2 and CH_4. A pilot scale (currently under realisation) and a full scale plant were designed from these data. This plant has a better capacity and utilisation if coupled with biogas upgrade to biomethane. The valorisation of CO_2 from biogas is integrated in the process by demonstrating the feasibility of a methanation reactor.

Preferred and 2nd choice for the topic: 1) CO2 utilisation and recycling; 2) Air cleaning and combustion
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Ruminants, mainly dairy cattle, are widely recognized as one of the main contributors to methane emissions in the environment, playing a significant role in the global warming phenomenon. Considering that a cow emits about 500 L/d of methane and in view of the increasing population of cows due to the intensive farming activities, the daily methane emission is considerable. It is estimated that a cattle (600 kg of body weight) consumes 21 kg DMI /day and due to the enteric fermentation and respiration releases 23 g CH_4 / kg DMI and 647 g CO_2 / kg DMI. Extensive efforts have been made to reduce methane emissions from ruminants prior to their release into the environment; however, considering that the enteric fermentation process is unavoidable, it is crucial to establish methods for capturing the emitted methane.

Given the common practice of implementing forced ventilation within barns for animal well-being, the discussed process aims to capture methane via adsorption on either synthetic or natural zeolites or different active carbons through the barn ventilation. Great limitations come from the Direct Air Capture of both gases due to their limited partical pressure and therefore low adsorption equilibrium concentrations.

The same two greenhouse gases coexist in the same productive frame as product of the anaerobic digestion of waste agro-zootechnical wastes. Therefore, the same adsorption system can be implemented efficiently also for the upgrade of biogas to biomethane, acting as a CO_2 capture technology. After saturation with the barn adsorption. The subsequent valorisation of the captured CO_2 to synthetic methane through the Sabatier reaction is then considered. These three integrated strategies offer the possibility to improve the sustainability of the zootechnical sector.

In this work, both experimental and process simulation methods have been coupled for the design of pilot scale plants and the relative scaled up design to full scale. Different options to improve the sustainability of intensive farming and biogas production and upgrade to biomethane have been designed and compared.

Materials and Methods

The adsorption isotherms of the gases on the selected adsorbent materials were first taken from the literature and then validated through experiments using a Hiden Catlab apparatus. Both saturation isotherms and dynamic breakthrough curves have been collected. Process design has been performed using Aspen Adsorption® V11 software after retrieving the relevant kinetic, transport and thermodynamic parameters. Different adsorbents have been exposed into a stable for 3-6-9 weeks in

different locations and then characterized by thermogravimetry and by temperature programmed desorption coupled with mass spectrometry.

Ni-based catalysts (5-20 wt%) supported over CeO_2, SiO_2, Al_2O_3 and ZrO_2 have been prepared by impregnation and co-precipitation. Testing has been done under practically relevant conditions at pressure up to 20 bar, with a stoichiometric H_2/CO_2 feed, considering the Sabatier reaction for the methanation of CO_2. Process design has been accomplished with Aspen Plus process simulator.

Results and Discussion

Carbon dioxide poses a significant challenge for methane capture on zeolites, because adsorption competition exists between CO_2 and CH_4. The adsorption process is dominated by the carbon dioxide adsorption. This revealed the necessity of a two-stage adsorption system, with two beds in series. An initial "guard bed" filled with zeolite 13X was used to adsorb carbon dioxide and other gases from the barn, while efficiently adsorbing methane in the second bed of the same volume filled with Clinoptilolite, a cost-effective natural zeolite with excellent properties for methane adsorption. With the current design configuration, the first bed reaches saturation in 210 days whereas the second bed reaches saturation in 40 days; consequently, five replacements need to be executed while keeping the guard bed in operation. The designed plant allows to obtain an exiting flow consisting only of air, therefore mitigating the environmental impact of the agricultural sector.

As for CO_2 utilisation, we considered a biogas production facility. H_2 is considered as produced from water electrolysis fed with renewable power. A key issue is the strong exothermicity of the reaction. Our research explores the use of water vapour, added on purpose to the reactor as a thermal vector and later condensed. The simplest and most economical reactor arrangement is composed of a certain number of adiabatic catalytic beds (up to five) with intercooling. Alternative arrangement has been explored designing a fluidized-bed reactor, that allows better temperature control, but this led to incomplete conversion and it was difficult to scale-up.

The possibility to use the methane already present in biogas as diluent (i.e. thermal vector to control the exothermicity) was also considered, offering the additional advantage to eliminate the otherwise needed and expensive CO_2 capture step.

This option is intended to improve the CH_4 yield and to meet the purity specifications for feeding the natural gas distribution grid. Possible poisons for the methanation catalyst, such as sulphides or nitrogen containing poisons, were considered and removed by the adsorption pretreatment. Two options were further considered, one with preliminary CO_2 separation from biogas and methanation of pure carbon dioxide, the other one with direct treatment of the biogas stream.

At least 4 reactive stages for the methanation reaction were needed to get > 75% conversion. Either adiabatic or cooled catalytic beds were compared, operating below 400°C.

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