Direct catalytic methanation of biogas – Part I: New insights into biomethane production using rate-based modelling and detailed process analysis

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A B S T R A C T

Direct methanation of biogas is a promising application of the Power-to-Gas concept, since up to 80% more methane can be produced in comparison to conventional biogas upgrading methods. Six different processes, in which a bubbling fluidized bed or a fixed bed technology serves as the main reactor, were designed, simulated in detail and evaluated in terms of technical feasibility and product gas quality. Both reactor types showed the same chemical performance, since they are both restricted by kinetic and thermodynamic effects. However, the cooled fixed bed reactor requires about three times more catalyst mass than the bubbling fluidized bed. Both methanation technologies did not reach Swiss or German high calorific gas grid requirements in one step. Further upgrading units are necessary which were often not considered in previous literature. Hence, the technological effort for biogas upgrading is higher than often stated in literature. With a subsequent second-stage fixed bed or a gas separation membrane, every process considered reaches the required product gas quality. It is more challenging to fall below the maximum limit of hydrogen (2 vol-%) than to reach the mandatory methane content for grid injection. The electrolysis clearly dominates the power consumption in all processes.

1. Introduction

The political objectives regarding the energy system in Germany and Switzerland contain phasing out nuclear power and increasing the share of renewable energies [1,2]. This resulted in Germany in three times more electricity production from renewable sources in 2015 (194 TWh) than in 2005 (63 TWh) [3]. In Switzerland, a share of 38% of electricity produced from nuclear power plants in 2014 is targeted to be compensated by renewable sources by 2050 [1,4]. Because of daily and seasonal changing conditions of wind, sun and water, renewable electricity production is subjected to fluctuations which have to be compensated by storage possibilities. A storage system should not only balance the electricity fluctuations between hours and days, but also between summer and winter. Therefore, storage possibilities at large scale will be required in future with a further increase of renewable electricity share.

The Power-to-Gas (PtG) system is one approach which may contribute to solve the storage problem caused by using renewable energies. The concept envisages the conversion of electrical energy to chemical energy in form of hydrogen or methane. These gases can be stored in the existing gas grid. However, due to Swiss gas grid

restrictions the share of hydrogen must be lower than 2 vol-%, thus methane is the targeted product gas with a minimum share of 96 vol-% [5]. The gas grid requirements in high calorific gas (H-gas) regions in Germany are similar [6]. In order to produce methane from hydrogen, a carbon source is needed, such as CO_2 from exhaust gas, wood gasification or anaerobic digestion of sewage sludge or green waste. Within this work, the concept of a PtG process integrated in a biogas plant was investigated in collaboration with the company *Energie 360°* in Zurich, Switzerland. The PtG process replaces the conventional gas upgrading unit (gas cleaning, CO_2 separation and drying) downstream of the anaerobic digestion. In Fig. 1, the scheme of the Biogas-PtG upgrade process is illustrated. Hydrogen is produced via electrolysis operated with renewable electricity. Biomass is converted in an anaerobic digestion step mainly to methane and carbon dioxide.

The biogas contains trace components like hydrogen sulphide, organic sulphur and siloxanes, which have to be removed in a gas cleaning unit before the biogas enters the catalytic methanation in order to prevent deactivation of the catalyst. Combined with hydrogen, carbon dioxide from biogas is converted to methane in a methanation reactor. Further upgrading of the gas is necessary in a subsequent purification unit to reach gas grid requirements. Thanks to the

a	specific mass transfer area, $m^2\,m^{-3}$		Y	yield, %
A	surface Area, m^2			
A_{cross}	cross sectional area, m^2		*Greek Letters*	
c	concentration, $mol\,m^{-3}$			
C_i	permeability constant of component i, barrer		α	heat transfer coefficient, $W\,m^{-2}\,K^{-1}$
c_p	specific heat capacity, $kJ\,mol^{-1}\,K^{-1}$		ε	void fraction, –
d	diameter, m		η	dynamic viscosity, Pa s
E_A	activation energy, $kJ\,mol^{-1}$		λ	thermal conductivity, $W\,m^{-1}\,K^{-1}$
G	mass flow, $kg\,s^{-1}$		ν	parameter for bubble rise velocity, –
h	height, m		ρ	density, $kg\,m^{-3}$
ΔH	heat of adsorption, $kJ\,mol^{-1}$		ψ	parameter for visible bubble flow, –
ΔH^0_{reac}	heat of reaction, $kJ\,mol^{-1}$			
k	reaction constant, differ		*Subscripts*	
K	adsorption constant, differ			
K_G	mass transfer coefficient, $m\,s^{-1}$		b	bubble or bubble phase
k_{Tref}	pre-exponential factor, differ		base	base case
m	mass, kg		e	emulsion/dense phase
$\dot{n}$	molar flow, $mol\,s^{-1}$		i	component index (H_2, CO_2, CH_4…)
$\dot{N}_{VC}$	bulk flow from bubble to dense phase, $mol\,s^{-1}$		j	differential element
Nu	Nusselt number, –		lim	limit
p	pressure, bar		m	reaction index; 1…Methanation, 2… Water Gas Shift
p_i	partial pressure of component i, bar		mem	membrane
Pr	Prandtl number, –		mf	minimum fluidisation
$\dot{Q}$	heat flow, kW		p	particle or pressure
R	ideal gas constant, $J\,mol^{-1}\,K^{-1}$		ref	reference conditions
R_i	rate of formation, $mol\,s^{-1}\,kg_{cat}^{-1}$		tot	total
r_m	rate of reaction m, $mol\,s^{-1}\,kg_{cat}^{-1}$			
Re	Reynolds number, –		*Abbreviations*	
s	effective thickness of membrane, m			
T	temperature, °C		BFB	bubbling fluidised bed
u	superficial velocity, $m\,s^{-1}$		FB	fixed bed
U	thermal transmittance, $W\,m^{-2}\,K^{-1}$		HX	heat exchanger
u_{mf}	minimum fluidisation velocity, $m\,s^{-1}$		Meth	methanation reaction
V	standard volume flow, $Nm^3\,h^{-1}$		Perm	permeate
v_b	visible bubble flow, $m\,s^{-1}$		Ret	retentate
V_m	molar volume, $Nm^3\,mol^{-1}$		SR	steam reforming
x	molar fraction, – or %		WGS	water gas shift reaction

integration of the PtG process into the biogas plant, synergies are created. Conventionally, carbon dioxide from the raw biogas is separated via CO_2 scrubbing or CO_2 membranes and is released as waste into the atmosphere. With the integration of the PtG system, no cost intensive CO_2 separation is needed; instead the whole raw biogas stream enters the PtG system. Here, carbon dioxide is considered as a valuable raw material within the PtG process and is converted to additional methane. Due to this procedure, the product stream increases by 40–80% depending on the carbon dioxide content of the raw biogas. Thus, biomethane production can be increased significantly with the same amount of biomass used, which results in a higher raw material efficiency. The catalytic methanation unit generates process heat which can be used for heat integration in the biogas plant or can be sold.

In the context of the storage of fluctuating renewable electricity flows, the processes in general should be able to operate in a dynamic mode. Polymer electrolyte membrane (PEM) electrolysers are able to start-up in the range of few minutes. The methanation reactors have start-up times of about 15 min from a stand-by mode. Both units are able to operate in full and partial load, so that it would be possible to compensate fluctuating energy flows.

Previous publications investigated PtG applications with biogas as the carbon source via simplified process models [7–11] which led to the neglect of important process units after the main reactor, i.e. the upgrading to fulfil the gas grid requirements. Often, only equilibrium models are applied for the catalytic methanation, which result in reaction rates close to complete conversion for lower temperatures
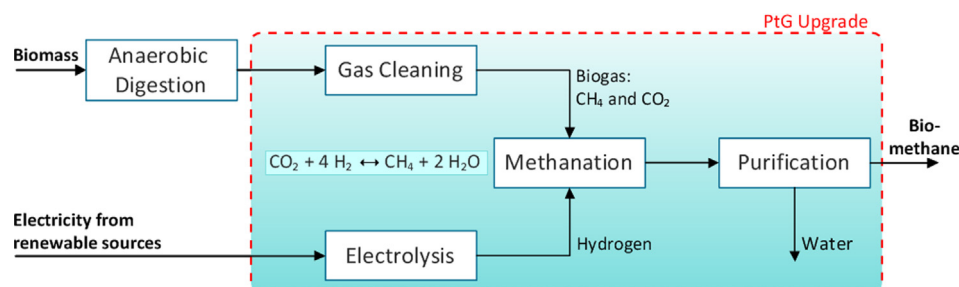

Fig. 1. Scheme of a PtG system integrated in a biogas process.