- VEGAZ PROJECT[†] -

TOWARDS A GREEN NATURAL GAS EFFICIENT PATHWAY THROUGH BIOMASS GASIFICATION AND METHANATION

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Abstract

The development of renewable energy is a major topic all over the world, in response to various environmental (reducing greenhouse gases emissions), geopolitical (reducing dependency on fossil fuels) and economic (developing new activities) issues.

Biomass gasification is a promising way to make renewable energy. It produces syngas which can be turned into different kinds of energy: CHP (Combined Heat Power), bio-fuel or combined **Biomethane fuel** (**BioSNG: a green substitute natural gas**) and heat. Combined Biomethane/heat is environment-friendly (high energetic and chemical yields, local heat valorisation, reasonable biomass supply and valorisation) and is complementary to the other renewable energies.

The so-called project "VEGAZ" which started in 2009 and which ends toward 2011, has studied deeply the combined Biomethane/heat pathway, in the case of gasified biomass. It is part of the industrial project GAYA made of a demonstration operation and an R&D platform on biomass gasification and its different valorisations. With a budget of 1.7 M€ and coordinating by the Research and Innovation division of GDF SUEZ, the project brings together four major players of French research on catalysis (UCCS), design and simulation of processes (CEA, GDF SUEZ R&D), thermodynamic, online measure (LSA) and gas separation (GEPEA).

The project has carried out technical, economical and environmental assessment between conventional and innovativ technologies for gas cleaning (scrubbers, fixed bed adsorption), catalytic methanation (fixed and fluidised bed reactors) and upgrading gas (Pressure swing adsorption, membranes separation and amines adsorption). The project has identified optimized configurations of these process blocks to produce a biomethane which could be injected into the natural gas grid and would be finally used as a "green" natural gas.

The first results show higher energetic conversion yields (Biomass to BioSNG) than the others 2nd generation biofuels production pathways (BtL, EtOH), starting with 56% already demonstrated at pilot scale to an energetic yield potentially reachable near 65% according to our simulations on commercial equipments (up to a theoretically 70 %). A comparative life cycle study of a virtual facility has been undertaken to assess the energetic balance and the potential environmental impacts of the whole process chain from the biomass production to the biomethane combustion. A full economical analysis has been carried out in order to prepare and to support the development of this innovative pathway in the natural gas economy.

The next step of the project is to be able to evaluate the combined heat/SNG path and prepare the development of the GAYA technology platform which will enable the Group GDF SUEZ to industrialize the process and then to generate and sell a "CO_2 free" natural gas, which will perfectly complement the natural gas offering.

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1. INTRODUCTION

The development of renewable energy is a major topic all over the world, in response to various environmental (reducing greenhouse gases emissions), geopolitical (reducing dependency on fossil fuels) and economic (developing new activities) issues. Sustainable energy sources have to be used in order to reduce greenhouse gas emissions. Biomass is currently the most important driver to reach the European objectives for the development of renewable energies.

Methane as the main component of natural gas is an important energy carrier and a raw material that is widely used in industry and households. For the generation of biomethane two conversion pathways are market mature, respectively, under strong development at the moment [1] the thermo-chemical biomass conversion (i.e. Bio-SNG (Synthetic Natural Gas)), (2) the bio-chemical biomass conversion (i.e. Biogas). The conversion technologies for Bio-SNG and Biogas differ significantly concerning, e.g. biomass feedstock, conversion principle, state of technology, average installed capacity per conversion unit, available technical experiences and still given R&D demand [2]. Both conversion routes have to provide biomethane fulfilling the requirements for a feed-in into the existing natural gas grid. Therefore, Biogas as well as Bio-SNG has to be upgraded by technical processes guaranteeing the same calorific value and chemical composition as natural gas. Only if this prerequisite is fulfilled biomethane can be used in any mixture with natural gas by using the same infrastructure without creating problems to the end user.

The state of technology for the production of SNG based on coal is market mature. Since 1984 in North Dakota a commercial-scale gasification plant is in operation. This plant converts lignite with a daily input of 18,500 t into SNG with an output of $4,247,520 m^3$ day ^{1} [3]. The conversion of biomass into Bio-SNG is not that far developed. Currently biomass gasification based on water vapour for the production of heat and electricity is successfully demonstrated and market mature; one plant is operating for several years in Güssing/Austria [4] and another plant is in its commissioning phase. But currently, a demonstration plant with 1MW gas capacity is has been carried out in 2009 and 2010 in Gussing by the PSI (Paul Scherrer Institute) CTU (Concept technology Universe). According to "economies of scale", conversion plants in the medium- to large-scale would gain market importance for an efficient production of Bio-SNG. Thus, according to current knowledge, the expected plant capacity will be in the range of 30–150 and more MW_{fuel}. For such Bio-SNG plants overall efficiencies from wood to methane are expected in a range of 60–70% [4,5,6,7].Therefore, both conversion routes complement one another in an ideal way. While the bio-chemical route uses wet biomass (e.g. animal manure, maize silage), and the thermo-chemical route focuses on solid biofuels (e.g. wood, straw). The former will be realised with plant capacities in the range of less than $10MW_{thermal}$ and the latter in the range of 10 to more than $100MW_{fuel}$. The product is basically the same and can be used in any mixture with natural gas.

Biomass gasification and methanation is a promising way to make renewable energy. It produces syngas which can be turned into different kinds of energy: CHP (Combined Heat Power), bio-fuel or combined **Biomethane fuel** (**BioSNG: a green substitute natural gas**) and heat. Combined Biomethane/heat is environment-friendly (high energetic and chemical yields, local heat valorisation, reasonable biomass supply and valorisation) and is complementary to the other renewable energies [7].

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adsorption). The project has identified optimized configurations of these process blocks to produce a biomethane which could be injected into the natural gas grid and would be finally used as a "green" natural gas **[11,12]**.

The GAYA project will enable the Group GDF SUEZ to industrialize the process and then to generate and sell a natural gas equivalent that is CO_2 free, which will perfectly complement the natural gas offering. This paper deals with the results of the exploration VEGAZ project on the downstream process chain after the gasification part.

2. BIOSNG PRODUCTION PATHWAY

The process line to produce bioSNG is made up of different process units. First the biomass feedstock enters in the gasification reactor. Biomass is changed into a gas called "syngas". This gas is composed with CO, H_2, CO_2, H_2O, CH_4 and tars. As the purpose of the process is to produce bioSNG, the part of methane in the gas composition has to be increased. In fact the syngas going out of the gasification step has a low CH_4 content. CH_4 is then produced in a methanation reactor. This is a catalytic reactor where CO and H_2 are changed into CH_4 and water. This reaction needs a catalyst, which can be damaged by sulphur contents and others inorganic compounds. So the syngas has to be very pure before entering this reactor. A cleaning step is therefore introduced between the gasification and the methanation reactor. At the end of this process line, the gas still does not have the right specificities to be introduced directly in the natural gas network. In fact CO_2 and sometimes H_2 and N_2 remain. So some gas separation units are installed such as a CO_2 removal unit, as well as an odorisation unit to obtain a gas with a composition close to the composition of natural gas and with the right specificities for the injection into the natural gas grids.

As the future GAYA R&D platform will be built to demonstrate the relevance of this entire process line, the VEGAZ project has been carried out in order to identify and optimize the best processes for each step of the conversion chain. The results carried out by GDF SUEZ and his partners in the VEGAZ are presented in this paper.

3. MODELLING AND ASSESSMENT OF THE BEST PROCESS CHAIN

Within the framework of the VeGaz project funded by ANR, two technical proposals of a process pathway for the production of bio - SNG (20 MW SNG scale) were studied: one from the Dutch research center ECN and another from the engineering company CTU. As CTU designed the pilot-plant in Güssing (1 MW_{SNG}), their feasibility study was based on their feedback.

CTU's feasibility study was chosen to provide the basis to build a model of the bio-SNG production chain.

This model was built with the Aspen Plus^{TM} software and takes into account the main following steps:

- Synthetic gas (syngas) cleaning;
- Syngas methanation in a fluidized bed reactor;
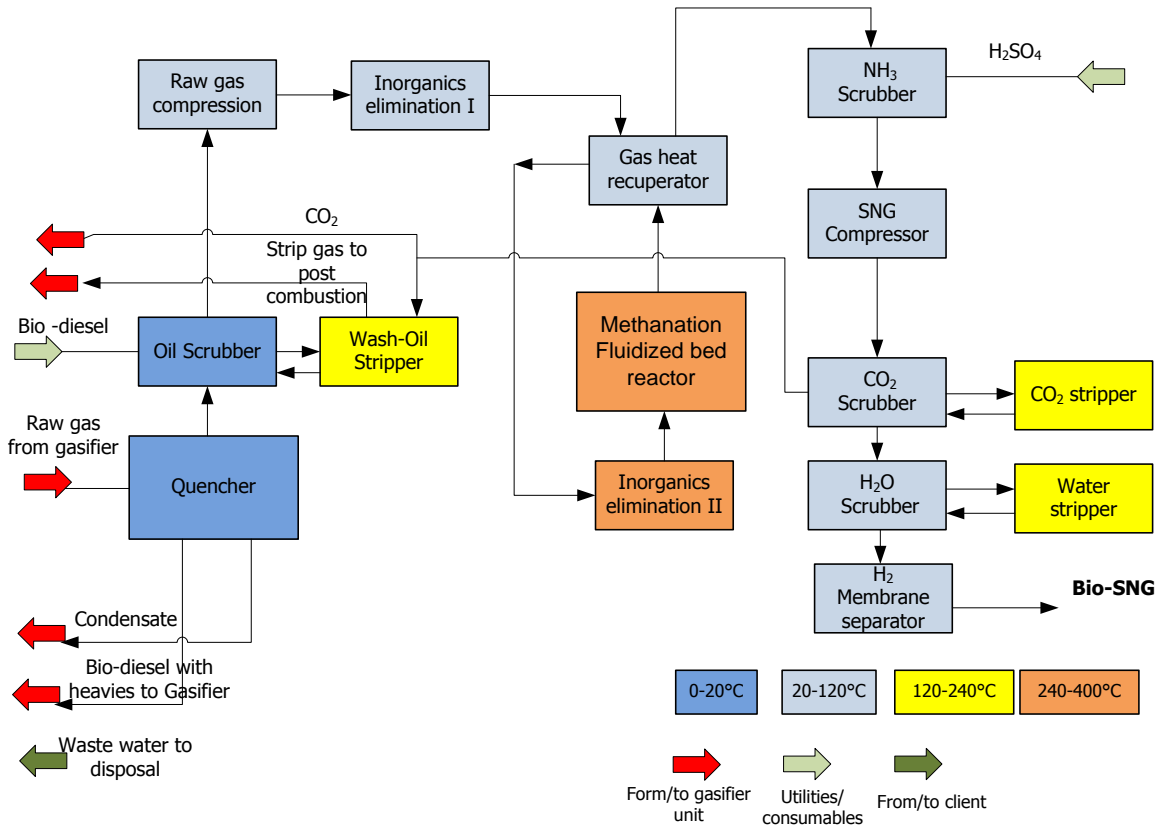- Bio-SNG upgrading in order to fulfil quality specifications for the gas transmission grid.

Figure 1 : Downstream process functional scheme

The simulations allowed a better understanding of the whole CTU process chain, and highlighted several possible improvements of its design. In a long-term view, modelling enhancements shall enable to carry-out detailed sensibility studies (technologies chosen for each operation unit , operating conditions, composition of synthetic gas, etc.).

In addition, this model already provides (for a given process flowsheet):

- Energy and Material balance figures;
- Data for cost estimation ;
- Data for life cycle analysis;
- A support for heat integration preliminary assessment.

4. SYNGAS CLEANING STEP: A TECHNOLOGICAL LOCKDOWN

At the outlet of gasifier the producer gas subsequently is cooled and filtered at 120-150°C. The gas then passes through a scrubber to wash out the heavy tars and partially condense water. RME (Rape seed oil Methyl Esther), also called biodiesel, is used as washing liquid. At the outlet of this pre-cleaning SNG is directed through a quencher. The quencher is used to cools down the SNG to around 10°C and condenses out most of the water that is present in the gas. For this purpose the liquid circulation loop of the quench scrubber is cooled by chilled water. Part of the recirculation liquid is fed to the decanter where the water phase is settled and removed through quench condensate collector. The waste water is sent to the gasifier where the organic contaminants of the waste water are incinerated.

The organic phase is fed back to the quench scrubber column. Downstream the quench scrubber an additional scrubber (called oil scrubber) is installed. The purpose of this scrubber is to further remove unwanted organic traces from the synthesis gas. The oil scrubber is operated with Biodiesel, wich is re-freshed and cooled by chilled water. The absorption liquid from the oil scrubber sump is sent to the oil stripper column where the absorbed organic compounds are removed at elevated temperature.

Downstream the tar scrubbing section the gas is compressed in a screw compressor from atmospheric pressure to around 3 bar and inorganic compounds are removed by passing through two fixed absorber. The first stage is fitted with doted activated carbon and is operated at 50 to 60°C. The second stage is fitted with ZnO and a chlorine catcher and is operated at 250 to 300°C.
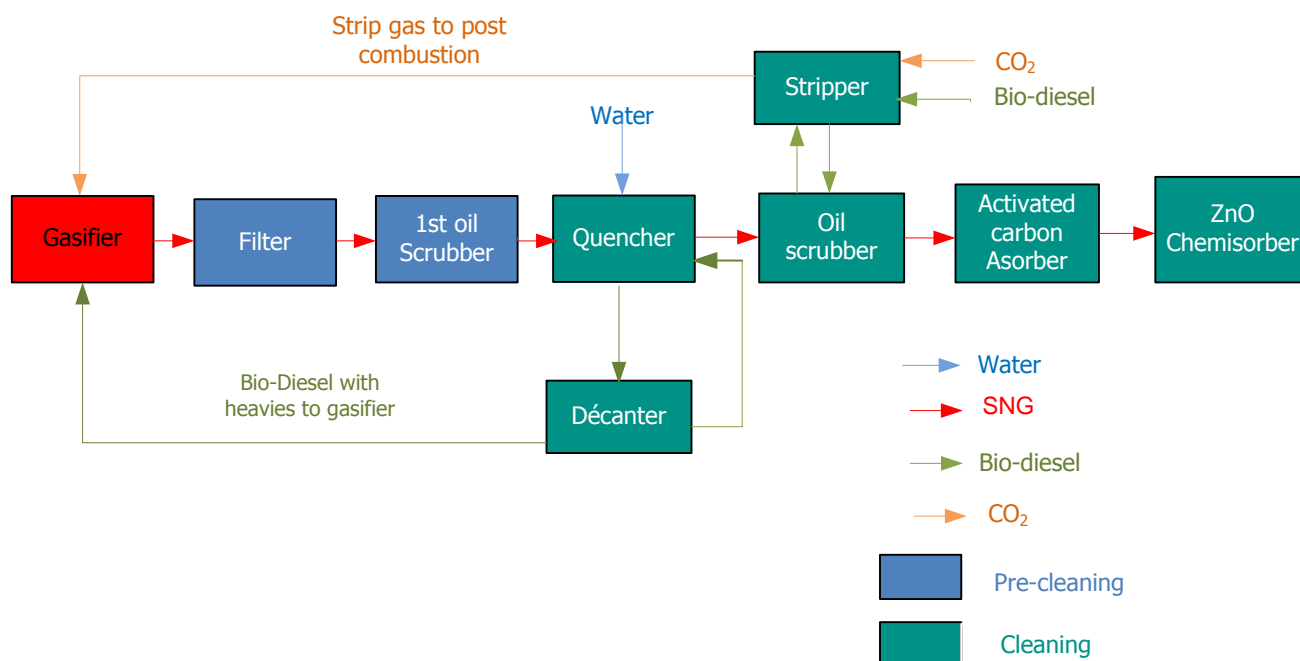

Figure 2 : syngas cleaning functional scheme

4.1 Optimization of SNG cleaning

  o **Objectives**

- Acquisition of equilibrium data and liq-liq liq-liq-vap (development and validation of the thermodynamic model)

- Identification of optimal conditions for removal of tar.

- Identification and assessment of the most efficient solvent

  o **Experimental procedure**

- 8 tar model compounds: Benzene, toluene, phenol, thiophene, pyridine, naphthalene, anthracene and phenanthrene.

- Solvents: 2 organic and natural solvent (methyl palmitate and methyl oleate) and 1 chemical solvent (paraxylene).

- Experimental temperatures: 30°C, 50°C and 70°C.

  o **Main results**

- After parameter regression model fits very well with experiment results (see figure aside which represent anthracene solubility in methyl palmitate).

- Temperatures below 50 ° C are recommended to improve tar scrubbing.

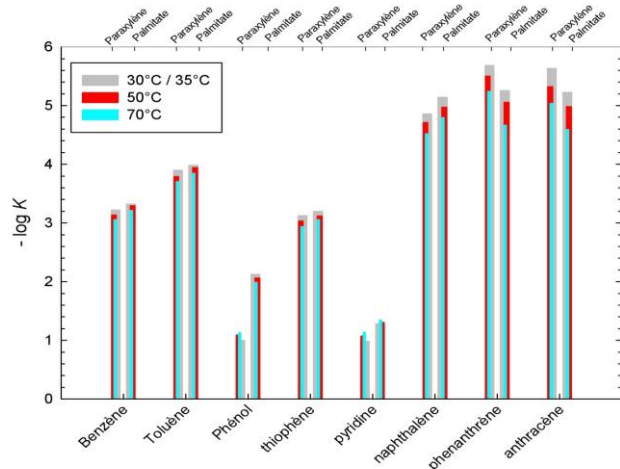Methyl oleate is recommended to improve tar scrubbing.

Figure 3 : results of tars scrubbing simulations

4.2 Simulation of SNG cleaning part

	CTU results	Simulation results
BENZENE	96,8%	97,9%
TOLUENE	96,8%	96,9%
NAPHTALENE	96,8%	100%
ANTHRACENE	5,0%	100%
THIOPHENE	95,0%	100%

Main results

- **Scrubber could purify at least 97 % of tars**

- Phenol and Pyridine are more difficult to remove.

- Heavy tars are best removed.

- Good efficiency for light tars.

Prospects

- Optimize the system hydrodynamics.

- Enlarge study to other families of compounds (tars, inorganic), based on accurate syngas sampling.

- Technical and economical optimization related to catalysts requirements.

5. CATALYTIC METHANATION FOR BIOSNG SYNTHESIS

Positioned after Syngas cleaning block, that allows the removal impurities and catalyst poisons formed during the biomass gasification step, the methanation process consists on the thermochemical catalytical transformation of syngas issues from biomass gasification in methane (bio-SNG – bio-substitute natural gas).

1.1 Methanation reaction fundamentals

Methanation is a highly exothermic and reversible reaction and is usually operated between 250 and 400°C for pressure levels comprise between 1 to 50-70 bars.

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H_{298K} = -206 \ kJmol^{-1} \qquad (1)$$

The methanation reaction has been deeply studied in a thermodynamics, kinetics and reaction mechanism point of view since that *Sebatier and Senderens* found in 1902 that this reaction is catalyzed by metals like Ni, Ru, Rh, Pt, Fe and Co) [13]. **Among all studied metals, nickel is the metal of choice due to its selectivity, activity and its price.**

From the thermodynamic point of view, methanation reaction is favored at low temperature and high pressure levels.

According to stoechiometrics ratio of methanation reaction (1), H_2/CO should be at least three or more. However, syngas mixture from biomass gasifiers has a H_2/CO ratio between 0,3 and 2, which is too low for a methanation reactor and a long catalyst lifetime. Moreover, lowers H_2/CO ratios can induce to carbon deposition on the catalyst which is responsible for its deactivation. That's way methanation reaction is accompanied by a side-reaction named Water Gas Shift which can be used as in-situ hydrogen source.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^{298K} = -41 \ kJmol^{-1} \qquad (2)$$

In a kinetic point of view, different mechanisms can be found in the literature for the methanation reaction. Deeply studied, since the 80's for coal gasification, and its valorization SNG, and more recently for biomass valorization pathway, it does not exist <u>one</u> accepted kinetic model approach for CO methanation. This can be explained by the particularity of this highly exothermic reaction in which each model proposed in literature must be interpreted according to the experimental conditions applied for each case, *i.e.*, temperature, partial pressure, reactor concept and nickel catalyst formulation.

1.2 Methanation processes

The firsts methanation processes were developed during the 50's and the 80's for a coal valorization. Some of them are, nowadays, proposed for biomass valorization. In parallel, new processes are under investigation for SNG production from biomass.

For bio-SNG production from biomass, we can consider two major categories of methanation reactors: fixed and fluidized bed reactors.

- Fixed bed methanation processes

In this category, two major industrial processes are mentioned: Lurgi process and TREMP^{TM} process from Haldor Topsoe. The first one, **the Lurgi process**, was the first commercial process for SNG production in pipeline conditions. The methanation unit is constituted by two methanation adiabatic reactors with internal recirculation and catalyst is supplied by BASF. A supplementary reactor is also needed for H_2/CO adjustment.

The fixed bed reactor process with internal recycle proposed by Haldor Topsoe, initially developed for a coal application, is today used for SNG production from biomass. Haldor Topsoe process named TREMP[TM] – Topsoe's Recycle Energy Efficient Methanation Process – particularity consists on the heat (heat produced due to exothermicity of the methanation reaction) recovery strategy and its valorization in high-pressure superheated steam. The temperature range of reactors is generally fixed between 250 and 700°C and the operation pressure can reach 50-70 bars. These temperatures levels ask for high-temperature resistant catalysts, which mean more expensive catalysts. In fact, simple nickel catalysts are very sensitive to high temperatures. Sintering phenomena can occurs which is responsible for irreversible catalyst deactivation.

The methanation units are constituted by 3-4 methanation reactors. A supplementary reactor is needed for H_2/CO adjustment (WGS reactor).
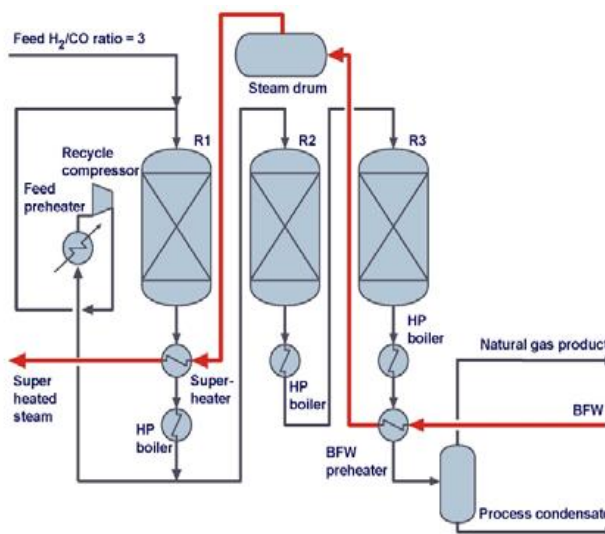
Figure 4: Fixed bed process proposed by Haldor Topsoe   **Figure 5: Fluidized bed process proposed by PSI/CTU**
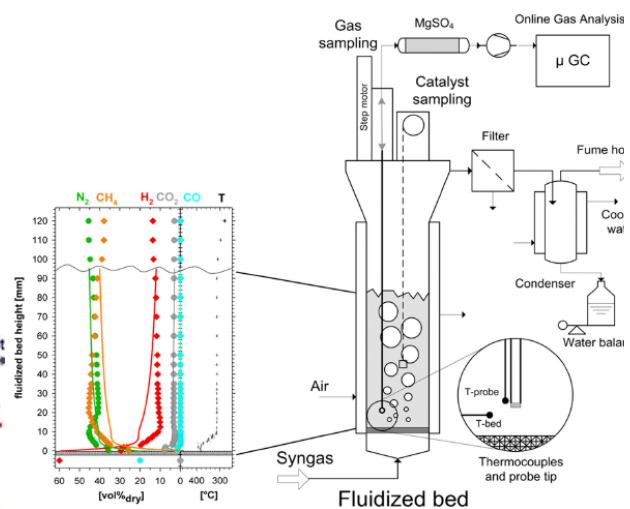
- **Fluidized bed methanation process**

Fluidized bed are known to be suitable for large-scale operations of heterogeneous catalyzed reaction with high exothermicity. The mixing of the fluidizing solids leads to an almost isothermal condition in the reactor, which allows simple and easy control of the operation. Heat and mass transfer is higher compared to fixed bed reactors. Easy remove, add and recycle catalyst continuously during the process is also possible with this reactor technology.

COMFLUX process developed in 1980 by Thyssengas GmbH, constituted by an internal heat exchanger fluidized bed reactor and operates in isothermal conditions due to the internal heat exchanger. The H_2/CO adjustment is performed in the same reactor, which means that one only reactor is required with this technology. Tested on pilot units during several hours were performed in the past allowing the production of about 11 millions of Nm^3 and 16 000 ton of superheated steam.

In 2006, PSI (Paul Scherrer Institut) decided to test a fluidized bed reactor (based on research results obtained during the 80's with COMFLUX for a coal application) in biomass valorization conditions. Results obtained were promising and COMFLUX was considered as the technology with optimum temperature control and the easier to scape-up to industrial size. The major problem associated to this kind of technology corresponds to the catalyst degradation and formation of fine particles that are responsible for the loose of catalyst and reactor performance decrease **[13]**.

In connection with the GAYA program, VEGAZ project, identified as a pre-industrial project, main goal was to study and characterize the most promising technologies associated to all steps of biomass valorization into bio-SNG chain process including the methanation one. Thus, activities were divided in two parts: the first one consisted on identifying the most adequate kinetic mechanism (kinetic law) in representatives conditions of an industrial process of biomass valorization into bio-SNG.

The second part of the work was attributed to the development of a reactor engineering model of a fixed and a fluidized bed reactor and to assess and compare the relative performance characteristics. These activities were under the responsibility of UCCS (Unité de Catalyse et Chimie du Solide of Lille University).

1.3 Main Results on catalytic methanation studies

- Looking for an optimized methanation kinetic law

According to literature, it is possible to find several papers proposing a different kinetic laws to methanation reaction using a catalyst presenting "industrial requirements" (nickel based catalysts). Methanation is an exothermic reaction and reaction is very fast, which difficult experimental handling and reactor conditions control.

Kinetics experimental measures were performed in a differential reactor type Micro-Berty (Figure 4). Methodology consisted of varying experimental conditions as temperature, total pressure, residential time, and reaction mixture composition representative of a syngas issue of biomass gasification (H_2, CO, H_2O and CO_2).

Figure 6: Micro-Berty reactor

Experimental device validation and catalytic tests were performed using an industrial catalysts containing 50% (wt.%) of nickel (reference catalyst) and a home-made supported catalyst containing 15% (wt.%) of nickel. According to preliminary results, tests should be performed with caution to ensure that reactor is operating under the kinetics regime (without any external or internal mass or heat transport limitations).

- **Effect of operating conditions on catalysts performances**

Figures 5 and 6 show the impact of H_2/CO ratio and CO_2 amount on reaction mixture on catalyst performances. Results show that the amount of hydrogen plays a very important role in CO conversion. In fact, the increase of H_2/CO ratio seems to improve catalysts performances. Moreover and according to supplementary tests and physic-chemical characterization results, variations of H_2/CO ratios inferiors to three lead to very important carbon deposition on catalysts which is responsible for catalyst deactivation.
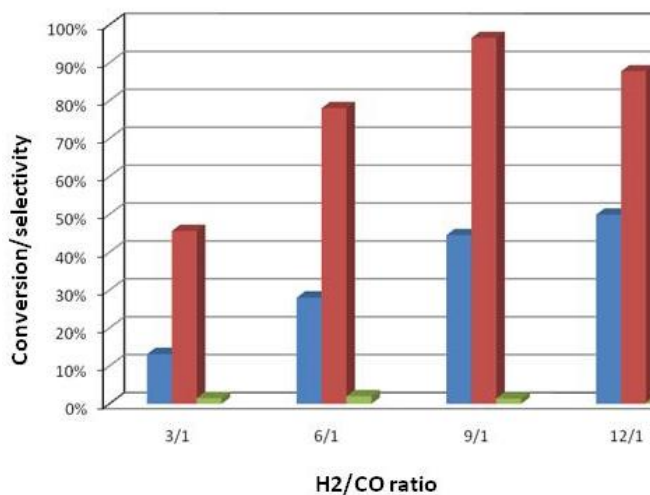

Figure 7: Effect of H2/CO ratio on CO conversion *(0.1,g of industrial catalyst, P = bar, T = 225 °C, Q_e = 20 Nml.min^{-1})*

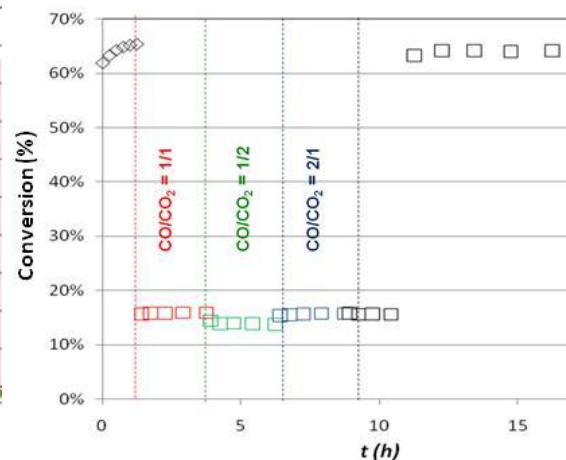**Figure 8: Effect of CO2 amount on CO conversion** *(0.1,g of industrial catalyst, P = bar, T = 225 °C, Q_e = 20 Nml.min^{-1})*

In what concerns CO_2 impact on catalysts performances, and according to Figure 6, initial performance of industrial catalyst is of about 65,7% (in the absence of CO_2 in the reaction mixture). The introduction equimolar amount of CO_2 in the mixture leads to a very important decrease of catalyst activity to 15%. It was also observed that the increase of the CO_2/CO ratio does not impacts the catalytic activity (same conversion for $CO_2/CO = 1$ or $CO_2/CO = 2$). The presence of CO_2 on kinetics reaction is hard to explain. Several explications are found in literature and most of them concerns the side-reaction of methanation of CO_2 [14].

The effect of pressure on kinetics was also studied. It was showed that pressure has a very important effect between 1 to 5 bars (CO consumption is three times faster at 5 bars than at 1 bar). However, no major effect is observed between 5-25 bars [15].

- **Kinetics laws modeling**

In order to find the most appropriate kinetic model that describes the different reactions occurring during the methanation process, experimental results were compared to those reported on literature. Among the several kinetic laws found in literature concerning methanation reaction, only those that used experimental conditions close to ours were chosen.
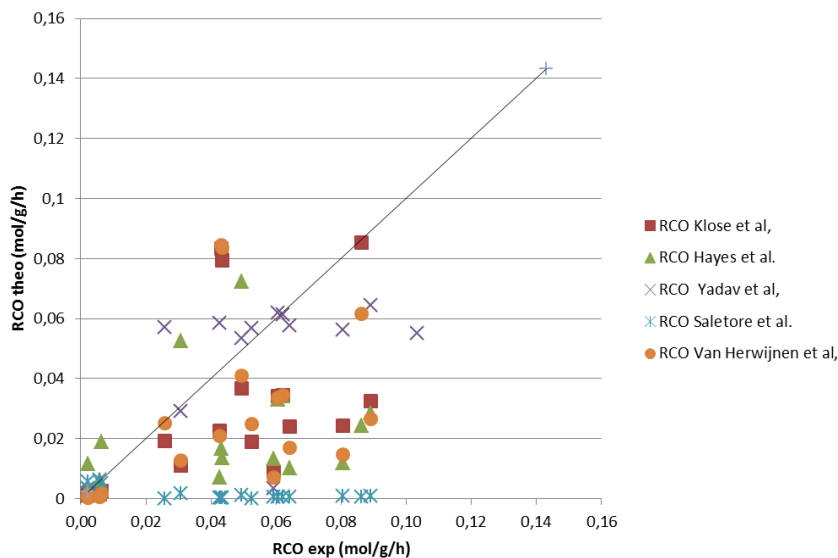
Experimental tests were performed in the following conditions:

- Industrial catalyst : 0.1<m<0.4h
- Temperature: 473K<T<523K
- Pressure: 1<P<20 bar
- Syngas composition: 2.5<H2/CO<19.5

Figure 9: Comparison between experimental and simulated data

According to all chosen models [16-22], *Klose et al.* [19] give us a kinetic law profile seems to be the most adequate to our operating conditions. According to this author, the limiting step corresponds to the formation of CH_2^* species on the surface of the catalysts during adsorbed CO and H_2 dissociation. Then, this kinetic law was modified in order to minimize experimental and simulated values. This optimized model was then introduced in both, fixed and fluidized reactor models.

1.4 Reactor engineering models

The work dealt with the development of reactor engineering model for the bio-syngas to methane process and to provide guidelines for the selection of an industrial Methanator. Reactor engineering model based on first principles of conservation of mass and energy was developed and performance of the reactor was studied under various operating conditions.
Fixed bed reactor (FBR) and Fluidized bed reactor (FluBR) were simulated as part of the study. Simulations were done for the typical pilot scale capacity of 56 mol/hr of CO fed to the reactor.

- External and internal mass or heat limitations

First of all, it was necessary to ensure that reactor is operating under the kinetic regime without any external or internal mass or heat transport limitations.
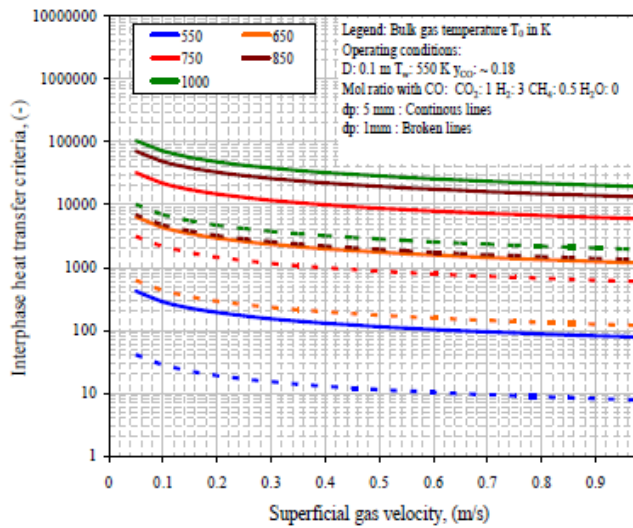

Figure 10: Variation of interphase mass transfer criteria with superficial gas velocity at different bulk temperature of the gas for 1mm and 5mm particles
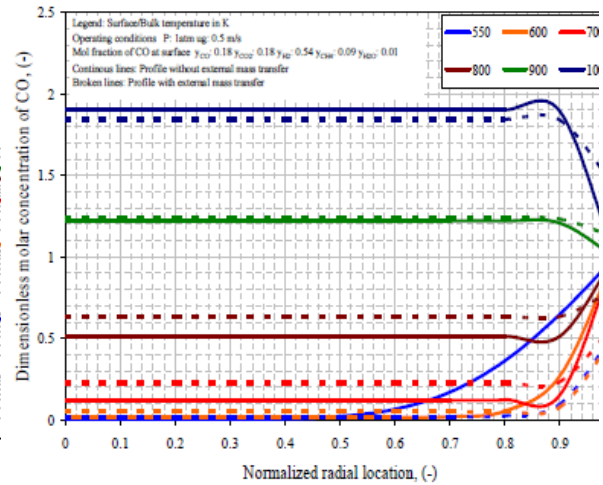
Figure 11: Dimensionless concentration profiles inside 5mm catalyst particle with and without external mass transfer effect and at different surface/bulk temperatures

Results show that severe interparticle, interphase heat and mass transfer and intraparticle heat transfer limitation in the reactor (Mear's criteria must be inferior to 1 to ensure that there are no limitations to mass and heat transfers). The severity of limitation would found to be high at higher temperatures. Thus, for typical fixed bed reactor with catalyst particle of size of size 5mm, the possibility of intrinsic kinetic controlled rate would be seldom realized.

Strong pore diffusion and external mass transfer limitation was observed for typical fixed bed catalysts of 1mm and 5mm size.

- **Comparison between fixed and fluidized bed reactors**

The complete description of gas solid fixed bed reactor (FBR) would involve use of the conservation of mass, momentum and energy balance for both the phases (gas and the solid) in the reactor. The phenomenological models can be broadly classified into pseudo-homogeneous models and heterogeneous models. The pseudo-homogeneous model does not take into account the presence of solid phase in the reactor and solves a single set of mass and energy balance equation for the gas phase. In the heterogeneous model, appropriate interphase terms are included to model the transfer of mass and energy across the gas and the solid phase. Each phase has a set of mass and energy balance equation.

In the other way, the fluidized bed reactor was modeled with the two-phase approach [14]. The reactor was operated as bubbling fluidized bed consisting of bubble and emulsion phase. The bubble phase consists of only gas and the catalyst concentration in the bubble was assumed to be negligible. Hence, no reaction was accounted in the bubble phase. The emulsion phase consists of gas and catalyst particles, where the reaction takes places exclusively. The pore diffusion within the catalyst particles was neglected, as catalyst particles were of the order of 100 μm and hence effectiveness factor was assumed to be 1 for the heterogeneous reaction with no external mass transfer effects.
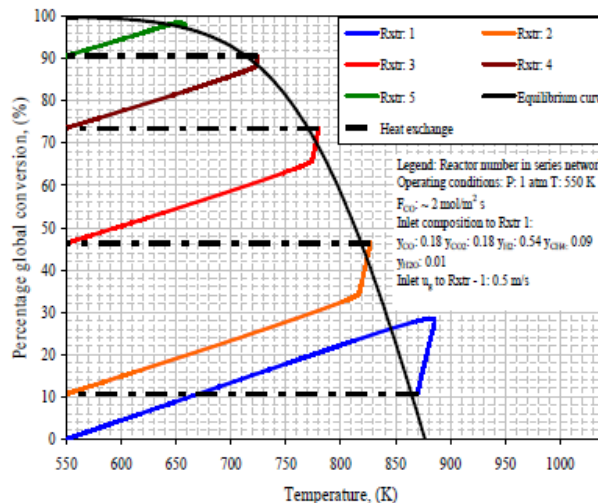
Figure 12: Percentage global conversion against temperature in the system of FBR in series with intermediate cooling
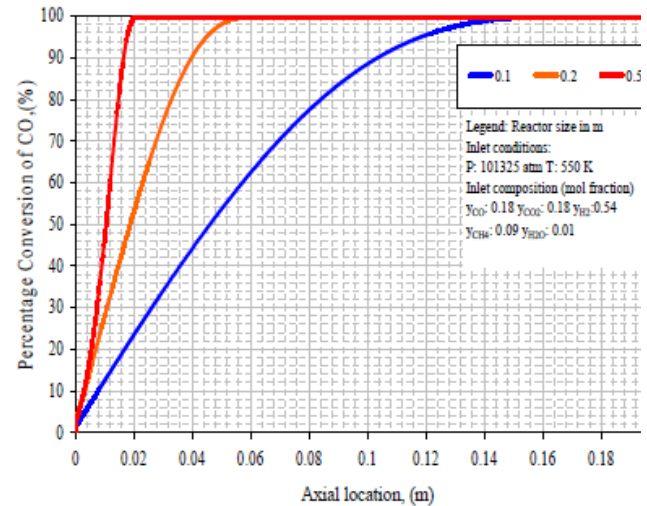
Figure 13: Percentage conversion of CO along the length of fluidized bed reactor of different sizes

According to results, the conversion in a single adiabatic reactor is limited by equilibrium. The maximum achievable conversion in a single reactor was limited to roughly 10% with temperature reaching the steady value of ~ 860 K. It was evident that in principle, the battery of FBRs can be simulated to increase the conversion in the methanation process and reach complete conversion of CO in the process.

The isothermal fluidized bed model was simulated for reactor of different diameters. One reactor seems enough for total CO conversion and increasing reactor diameter leads to a faster total conversion of the reactive.

The following table resumes the main results obtained during the several simulations performed with both models:

Table 1 : Consolidated comparison of different options for methanator reactor

| Reactor	% CO Conversion	Relative catalyst inventory	GHSV (m^3_{gas}/m^3 cat hr)	WHSV (kg_{gas} / kg_{cat} hr)
Adiabatic FBR without external mass transfer and pore diffusion resistance ($\eta = 1$)	11	1	12E5	~200
Adiabatic FBR with external mass transfer and pore diffusion resistance	13	350	3600	0.7
Isothermal FBR at 550 K	99	35	32E3	6.7
FBR with external wall cooling U 100 W/m^2 K and T_{wall} 500 K	99	150	7600	4.7
FluBR at 550 K	99	12	13E5	~200

1.5 conclusions on the catalytic methanation step

The comparative study performed with fixed and fluidized reactor models leads to the following conclusions:

- The choice of fixed bed reactor was not found to be an attractive option for the methanation process with the kinetics based on the proprietary industrial catalyst. Significant pore diffusion and external mass transfer limitations were found for a typical fixed bed catalyst size of 5mm and 1mm.
- The option of non adiabatic fixed bed reactor with external wall cooling was found satisfactory to overcome the equilibrium limited conversion of adiabatic reactor. Choice of equilibrium limited fixed bed reactors with intermediate heat exchange was also found feasible option to overcome the equilibrium limitation of adiabatic reactor.
- Fluidized bed reactor was found to be most promising reactor choice for the methanation process with less catalyst inventory. The fluidized bed reactor was found to be attractive in comparison with all operations modes of fixed bed reactor like adiabatic, isothermal and fixed bed reactor with heat exchange.

6. BIOSNG UPGRADING STEP: A KEY PROCESS TOWARDS INJECTION IN NATURAL GAS GRID

In order to inject bio-SNG in natural gas transport and distribution grids, its quality must be adjusted after methanation to fulfil grid specifications (especially HHV and Wobbe Index). Bio-SNG upgrading can be achieved through three main separation stages (see figure below). VeGaz project mainly focused on CO_2 and H_2 removal.
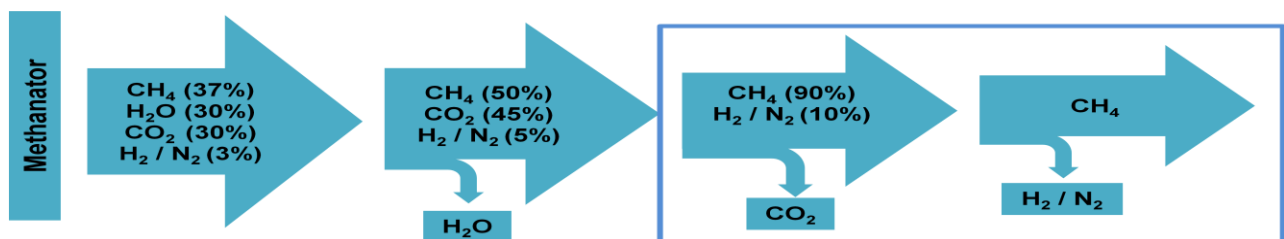

Two different upgrading pathways were studied and compared technically and economically:

1. Amine scrubbing for CO_2 removal followed by a H_2 separation membrane: This configuration is operating in Güssing pilot plant, a feedback being available.

2. Two series PSA units (see figure aside) :

   This configuration was first evaluated at a laboratory scale by GEPEA[1] research department in Nantes. These experiments aimed at identifying the most suitable adsorbents and operating conditions (adsorption and desorption pressures, cycle duration) for each separation stage. Besides they provided data to build a model and size an industrial unit.
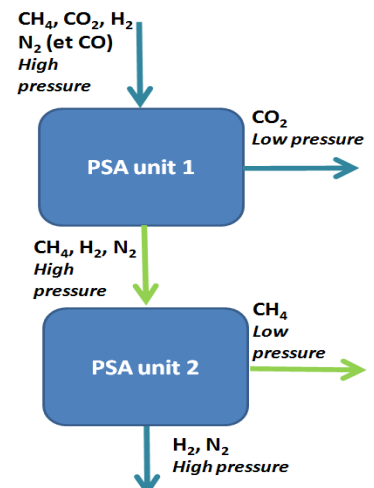
6.1 Experimental and techno-economic assessment for CO_2 removal

- **PSA process**

   Among five adsorbents initially selected by GEPEA, two have shown particularly good performances during experiments: a zeolite (Z13X) and a carbon molecular sieve (CMS FB 1.8). The

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[1]Génie des Procédés, Environnement, Agroalimentaire.

positive effect of minor compounds on methane recovery rate was also demonstrated by comparing PSA cycles tested with bi-component (CO_2/CH_4) and multi-component ($CO_2/CH_4/H_2/N_2$) gases.

A dynamic model of PSA was developed in MATLAB[TM] Its parameters were adjusted by using GEPEA experimental data. Then, **performances of Z13X and CMS at industrial scale were extrapolated with the model**. The industrial sizing of the corresponding PSA plants was optimized thanks to Parametric studies. Eventually, costs were estimated, enabling to select the most suitable adsorbent for CO_2 removal. The approach is summarised in the figure aside. Main techno-economic results are given in table below.
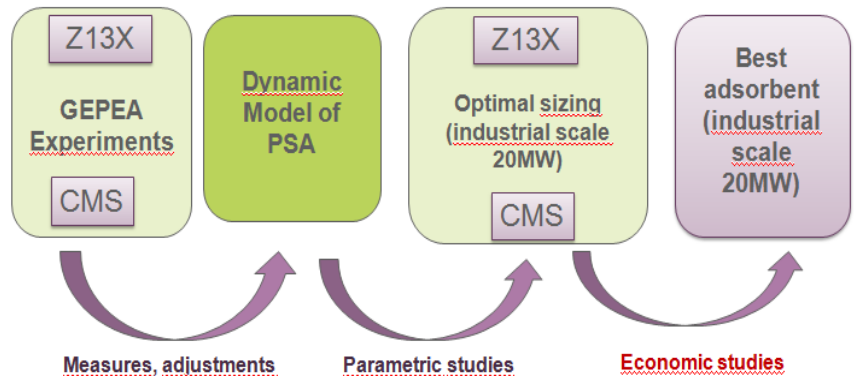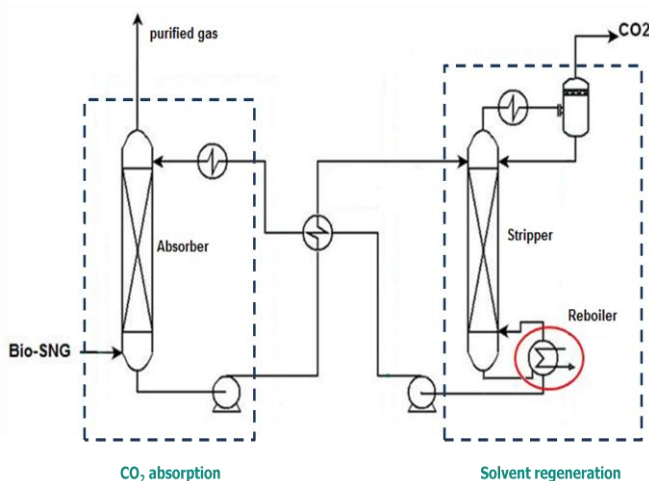

Table 2 : results of experimental sorbents comparison

	Z13X	CMS FB
Technical performances		
Adsorption / desorption pressure (bar)	3 / 0,1	3 / 0,2
Required quantity of adsorbent (m^3)	63,5	**18,5**
Vacuum pump power (kWe)	640	**300**
Duration of one cycle (s)	2345	360
Methane recovery rate (%)	90,6	**91,5**
CO_2 elimination rate (%)	97,2	97,1
Economical performances		
CAPEX (M€-2010)	**6,2**	**4,3**
OPEX (M€/year)	**0,77**	**0,53**

At industrial scale, the CMS FB 1.8 appears to be the best adsorbent to perform the CO_2 separation from raw bio-SNG. The modelling was performed for a simple PSA cycle and a bi-component (CO_2/CH_4) assumption. However, experiments and calculations showed that methane recovery rate could be increased up to ~96% due to effect of H_2 and N_2 in real bio-SNG, and thanks to PSA cycle improvements, such as partial recycling of the desorbed stream.

- **Amine scrubbing process (MEA-based)**

Simulation, energy optimization and sizing of the industrial MEA scrubbing process were performed using the Amine Package of HYSYS[TM] software.

This process has demonstrated high methane recovery rate (99%) and CO_2 elimination rate of (98%).

Cost was estimated with the same method as for PSA process. **CAPEX are estimated to 2.2 M€-2010**. Furthermore, the required reboiler duty can be fully provided by recycling heat produced in the methanation and gasification stages, thus reducing significantly **its operating costs.**

- **Comparison between PSA process with CMS FB and MEA scrubbing process**

At the end of this preliminary study, amine scrubbing appears to be more efficient and profitable to remove CO_2 from bio-SNG. **This conclusion is very specific to biomethane production by gasification and methanation of biomass,** due to the large amount of heat produced by the SNG plant and recycled in the amine regeneration system.

	PSA-CMS FB	Amine scrubbing
Depreciation (M€/year)	0,44	0,27
OPEX (M€/year)	0,53	0,20
Specific cost (€/MWh)	**4,6**	**2,2**

6.2 2nd upgrading stage: Limited comparison between PSA and membrane for H_2 removal

Three activated carbons (AC) were tested by GEPEA laboratory to adsorb CH_4 at pressures ranging between 20 and 30 bar. Among them, the commercial AC-SC and a novel AC manufactured by Jean Lamour Institute of Nancy (« AC-Nancy ») demonstrated satisfactory separation performance.

The following table compares the optimised laboratory-scale PSA cycle run with « AC-Nancy » with a polymeric membrane (based on Güssing experience). However, only limited conclusions can be drawn from these data, because of scale difference, and further optimisation prospects and costing which are still lacking.

Table 3 : comparison of PSA and polymeric membrane on gases separation efficiency

	PSA with AC-Nancy (GEPEA test)				Polymeric Membrane			
Operation pressure	30 bar Raffinate (H_2); 30 bar Bio-SNG feed; PSA; 1 bar Extract PRODUCT - CH_4 (desorption)				1.3 bar PERMEATE (H_2); 9 bar Bio-SNG feed; MEMBRANE; 9 bar PRODUCT (CH_4)			
Outlet SNG composition	CH_4 96.1%	CO_2 0.5 %	H_2 2.3 %	N_2 1.2 %	CH_4 96 %	CO_2 0.2 %	H_2 0.7 %	N_2 2.1 %
Recovery rate	CH_4: 70%		H_2: 46%		CH_4: 80%		H_2: 89%	

Both processes have comparable separation performance. However membrane would be favoured because of its lower operation pressure and higher delivery pressure. CH_4 losses are high for both processes: the H_2-enriched stream still contains ~70-75% of CH_4. A further treatment or an optimized recycling of this stream must be considered.

According to these conclusions an upgrading solution based on combined CO_2 and H_2 removal with a membrane shall be assessed in further studies.

6.3 Heat and mass integration with the whole SNG production process chain

The thermochemical chain produces important quantities of heat along with bio-SNG (gasification and methanation stages). Depending on the SNG plant situation, heat can be sold to neighbouring industrial plants. For the CO_2 removal stage, depending on specific favourable commercial conditions (steam price and demand), a PSA could be more profitable than an amines plant.

The CO_2 and H_2-enriched waste streams can be integrated from the upgrading process unit into other stages of the SNG production chain (CH_4 losses thus being valued). Beyond the optimization of the removal process itself, **mass and heat integration improvements can play a significant part in the cost and energy efficiency of the SNG plant [23]: it will be a core issue for future research works on SNG upgrading.**	*Possible recycling pathways of the streams depleted by the upgrading process*	
	CO_2 removal	*H_2 removal*
	• Stripping gas (tar removal stage) and combustion (gasification stage), thermal benefit still to be confirmed. • Inerting gas[2]	• To methanation • Recycled within the membrane or PSA • Combustion (gasification stage)

7. GLOBAL MODELLING BIO-SNG PATHWAY AND PROSPECTS

Gasification and methanation steps produce high and low temperature heat which may be integrated to the process or purchased as steam (by neighbouring industries, for instance). **Heat production and energy needs of the SNG process chain are strongly influenced by biomass characteristics**, in particular moisture (with a possible preliminary wood drying process), and lower heat value.

The diagram aside shows heat duty and production by the process for four different biomass types (for a 20 MW SNG-plant).
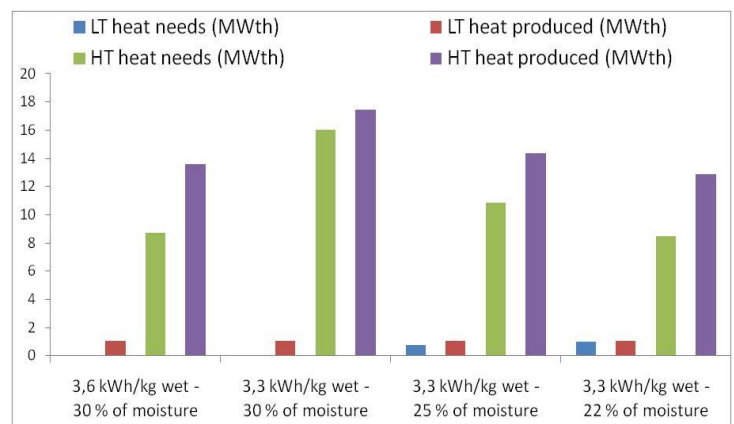
Figure 14 :basic energy integration on the whole process chain.

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[2] Only feasible if the depleted stream has a high CO_2-purity (especially for high temperature inerting, to avoid flamability).

For a hypothetical case with no heat integration, energy yield ranges from 45 to 60% [24 & 25]

Basic heat integration was studied and it was shown that it could improve the energy yield, up to60%, in particular when the exceeding produced heat (after heat recycling in the SNG plant) was valued commercially.

However, further R&D works shall be carried out to assess more precisely the technical feasibility of heat integration loops and validate or improve this result [25]
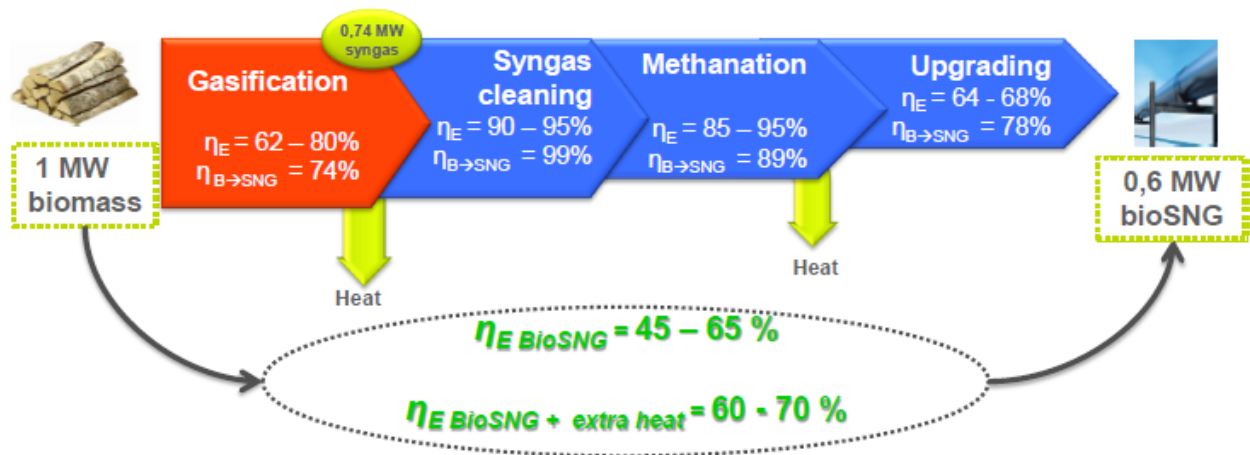

Figure 15 : Energy efficiency for the whole conversion process chain

8. THE LCA, A COMPREHENSIVE TOOL TO ASSESS THE BIO-SNG SUPPLY CHAIN

The Life Cycle Assessment – or LCA - is a standardized methodology, defined by ISO 14 040 and 14 044.

It is a systematic compilation of energy consumptions, raw material utilization and emissions to the environment (air, water, and soil) of a given system (product, service or organization) from raw material extraction to its end-of-life, including its production, utilization and all transportation phases.

The LCA method is composed of 4 steps and allows:

- Identifying the hot spots of the system from an environmental point of view and the improvement opportunities;
- Avoiding a pollution shift from one step to another or from one impact to another.

The main goal of this study is to realize a simplified assessment of the environmental burdens of the supply chain and final use of the Bio-SNG. The impact indicators considered are: climate change, eutrophication, acidification and non renewable energy consumption.

8.1 The biomass conversion, the main contributing step of the whole life cycle

The biomass conversion (gasification and methanation) is the main contributor of the whole life cycle with more than 55% of all impacts.

These results can be explained by the fact that:

- More than the third of the eutrophication and the acidification (38% and 35 %) are attributable to the direct emissions of gasification (NOx and SOx);

- The rapeseed biodiesel consumption, used for the syngas scrubbing, has a significant contribution to eutrophication and acidification (43% et 25%), due to its conventional agricultural origin;

- More than 35% of the non renewable resources consumption are due to the process electricity consumption, especially for the compressors (81 % of the total consumption).
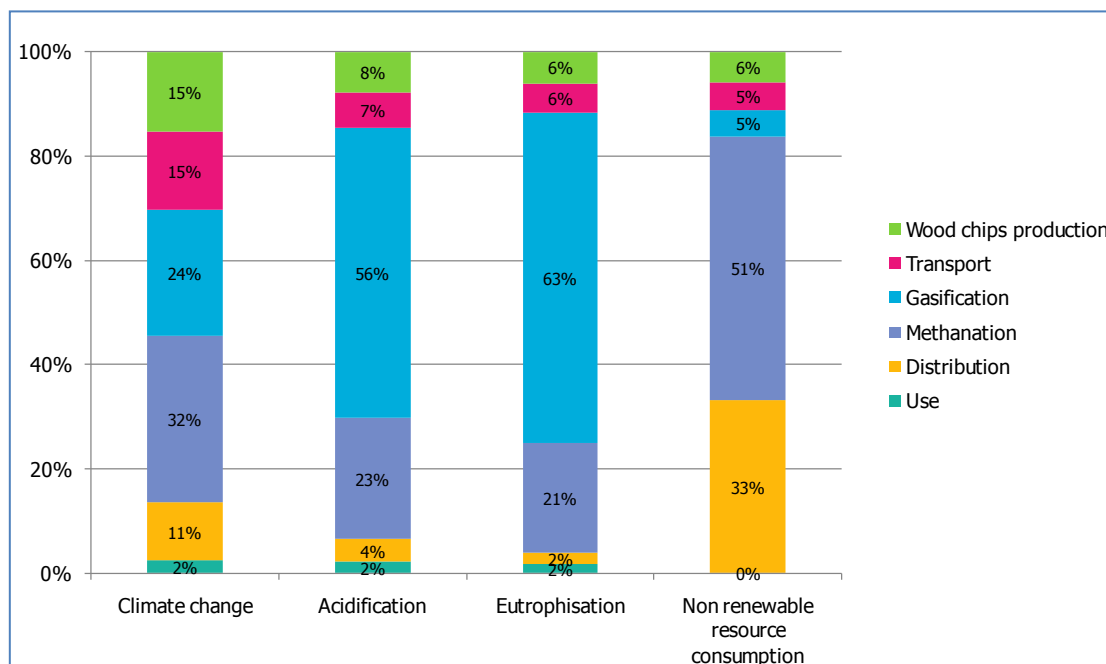
Figure 16 : Contribution of the different stage of the life cycle to the impacts

8.2 A greenhouse gases emissions balance satisfying the Renewable Energy Directive 2009/28/EC of the European Parliament and Council [

The two following scenarii have been compared:

- Reference Case : Bio-SNG production with heat integration to cover the needs of thermal process without external valorization of the remaining excess;

- R&D Goal : Bio-SNG production with heat integration to cover the needs of thermal process and external valorization of the remaining excess.

The comparison of these two scenarii shows that an external valorization of the excess heat can significantly reduce the impacts with up to -26% for the climate change. Thus, it seems to be interesting to valorize the heat excess when local conditions are favorable (for example if the conversion plant is near from industrial sites).

Furthermore, the greenhouse gases emissions of the Bio-SNG supply chain have been compared with the European Directive 2009/28/EC data regarding second generation liquid biofuels. The criteria fixed by this

directive for the GHG emissions reduction related to biofuels (as compared to the reference fossil fuel) are -35% in 2013 for existing plants and -60% in 2018 for newly installed plants.

The results show that the bio-SNG supply chain is compliant with the directive criteria with respectively 78% and 83% of greenhouse gases emissions reduction for the reference case and the R&D goal. Moreover, the environmental performances of the bio-SNG are globally very satisfying, but are less high than the BtL supply chain, as described by the data in the Directive.

Nevertheless, the results of this comparison are to be handled with caution because the assumptions and models are not strictly identical between the calculations carried out on the SNG industry on the one hand (VEGAZ project) and the default values and from the Directive for other biofuels on the other hand.

In conclusion, the first results of this first study are very promising from an environmental point of view. These resultants will be completed later in a further study, planned in the research project GAYA, which is coordinated by GDF SUEZ and aims to develop new technologies for producing second generation biofuels from biomass.
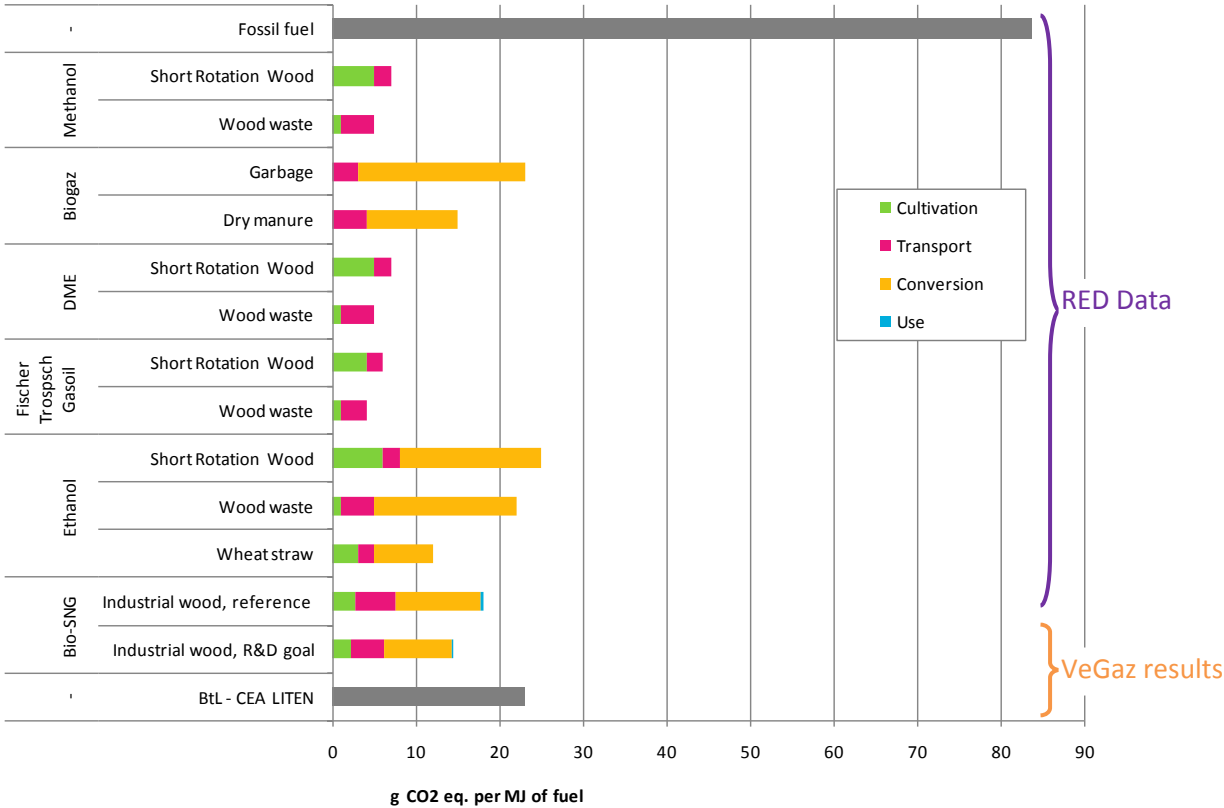
Figure 17 : GHG emissions of different biofuels

8. CONCLUSIONS AND PROSPECTS

Biomass, the third world primary energy source after coal and oil, represents the biggest potential for renewable energy. The thermo-chemical conversion of biomass into renewable natural gas (bio-SNG) by a gasification/methanation pathway is nowadays considered as a high-potential solution and complementary to traditional biomass valorization.

Contrary to the developments in the 80's with respect to methanation processes for a coal application, targeting large units, the Bio-SNG route, in France and in some European areas, focuses more on

decentralized plants of small and medium capacity in a technical, economic and environmental point of view. This capacity leads to the choice of a fluidized atmospheric gasification unit.

The VEGAZ project leads to identify the best process option in order to launch the demonstration project GAYA. Experimental and numerical studies have been carried out on the cleaning gas part of the process and demonstrate the very good efficiency of such process on the syngas pollutants like tars. The efforts must be now focused on the optimization of inorganic compounds removal and on hydrodynamics optimization of the scrubber. The work on methanation shows strong difficulties to obtain kinetics law at lab scale but leads to the main result that the methanation reaction is driven by thermodynamics and is not limited by kinetics. According to the numerical studies, the fluidized bed technology shows great advantages for small and medium scale BioSNG production units. Thus, the upgrading part is still complex and a global approach need to be carried out in order to choose the best option in terms of efficiency, energy consumption and economics.

The global simulations confirm the very promising efficiency of the pathway with a minimum of 45 % up to 65 % of energy conversion from biomass to BioSNG. These results confirm the pilot scale (1 MW_{bioSNG}) demonstration results from Güssing that provide in 2009 a 56 % of global energy yield.

The life cycle assessment confirm that this 2nd generation pathway has a very low impact on green House gases emissions and provide to GDF SUEZ a strong tool to drive the R&D process.

Moreover, the results of VEGAZ Project leads GDF SUEZ to prepare and launch the demonstration GAYA project in 2010 and 2011. The GAYA pilot platform will be commissioning in 2013 and will provide to GDF SUEZ a flexible tool in order to test and confirm these primary results and prepare industrialization of the BioSNG pathway towards 2015.

Acknowledgment:

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