



Energy research Centre of the Netherlands

Benzene and ethylene in Bio-SNG production:

nuisance, fuel or valuable products?

L.P.L.M. Rabou & A. van der Drift

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Benzene and ethylene in bio-SNG production: nuisance, fuel or valuable products?

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Abstract:

Gasification of biomass with the aim to produce Substitute Natural Gas (SNG) is best performed at temperatures around 850°C, where 50% of the combustion value of the producer gas is concentrated in hydrocarbons. After removal of the heavy hydrocarbons (i.e. tar) and sulphur components, the producer gas can be converted catalytically to a mixture of mainly methane, carbon dioxide and water. Using producer gas as intermediate instead of syngas can lead to 10% higher efficiency, as producer gas does contain a significant amount of methane already and because less heat is evolved in the conversion of the remainder than for a mixture of carbon monoxide and hydrogen.

Some of the hydrocarbons in producer gas, notably benzene, toluene, acetylene and ethylene, together with some of the more volatile tar compounds, can be a nuisance in the conversion step, as they easily form carbon deposits on the methanation catalysts involved. Several strategies can be followed to make these annoying components useful. Here, we will focus on benzene and ethylene, as each represents nearly 90% of the total amount of aromatic and unsaturated hydrocarbons respectively in biomass producer gas.

One approach, followed in the SNG demonstration plant in Güssing, is to remove benzene nearly completely from producer gas in a low-temperature scrubber. Recovered benzene with some of the scrubbing liquid is used as fuel to provide heat for the gasifier. Any benzene remaining in the producer gas and ethylene are converted in the fluidized bed methanation reactor. The fluidized bed creates conditions in which carbon deposits are gasified before they can harm the catalyst performance. The use of benzene as heat source in the gasifier reduces the need to burn part of the producer gas for that purpose. Effectively, more "clean" producer gas becomes available for the methanation step.

The MILENA type gasifier developed by ECN has a lower heat demand than the Güssing FICFB gasifier. Consequently, it has no use for benzene as an additional heat source. That is why ECN research focuses on solving problems associated with the conversion of benzene and ethylene to methane. One of the problems is removal of organic sulphur compounds, especially thiophene and its derivatives like benzo-thiophene. The main route pursued by ECN is conversion of thiophenes by a hydrodesulphurization (HDS) catalyst, followed by adsorption of the hydrogensulphide produced.

Benzene removed from producer gas by liquid scrubbing or adsorption to a solid sorbent can also be recovered for use as fuel in a separate boiler. An advantage of that approach would be that benzene can be stored more easily than producer gas to match heat production with demand by e.g. a district heat system or to provide heat during gasifier maintenance. In fact, that would copy the approach followed in Harboøre with tar.

Another promising option is cryogenic separation of producer gas. In principle, that would make it possible to separate and recover not only benzene but also ethylene. Even without purification, these may have more value as chemical base materials than when used as fuel. The cryogenic treatment would probably also capture sulphur compounds, thus considerably simplifying the gas cleaning needed for protection of the methanation catalyst.

Advantages and disadvantages of the above options will be discussed. Experimental results of ECN research on hydrodesulphurization and adsorbents will be presented. Further research questions will be addressed.

1. Introduction:

In present-day society fossil fuels are essential to provide people with food, healthy living conditions, comfort and wealth. Increasingly, we become aware of the shadow sides: the threat of climate change caused by the rising CO₂ level in the earth atmosphere, dwindling supplies and the risk of conflicts over the access to these supplies. Reducing, and ultimately abolishing, our dependence on fossil fuels requires a huge efficiency improvement and the development of other, sustainable, sources of energy and base materials.

The Energy research Centre of the Netherlands (ECN) is developing high-level knowledge and technology for a sustainable energy system. One of the research items is technology development for the production of Substitute Natural Gas from biomass (bio-SNG). Given the large share of natural gas in the Dutch energy consumption, the contribution of bio-SNG in the Netherlands is expected to rise quickly and surpass the share of solid biomass in heat production within the next decade [1].

The production of bio-SNG starts with the conversion of biomass into syngas or producer gas. Here, syngas means a gas mixture with mainly CO and H₂, and producer gas a mixture of CO and H₂ with methane and other hydrocarbons. Other components usually present are CO₂, H₂O, N₂ and various other compounds containing nitrogen, oxygen, sulphur or chlorine.

Producer gas is obtained by gasification at relatively low or medium temperatures, i.e. between about 700 and 1000°C. Syngas can be produced by gasification at high temperatures, usually above 1300°C, or from producer gas by a (thermal or catalytic) treatment which breaks down hydrocarbons into smaller molecules. Syngas is preferred for the production of chemicals and liquid fuels. Producer gas is advantageous for SNG production

because of its substantial hydrocarbon content [2]. Some of these hydrocarbons require special attention, to prevent them from hindering or even deactivating the methanation catalyst. The present article is limited to a discussion on hydrocarbons containing 2 to 8 C-atoms. How to handle heavier hydrocarbons (tar) is described e.g. in [3, 4].

2. SNG gasification technology:

A review of the technology developed for the production of SNG from coal and biomass can be found in [5]. Application was limited to one prominent example, the 3 GW Great Plains Synfuels plant which started operation in 1984 and produces 4x10⁶ m³/day SNG from lignite (www.dakotagas.com). Further plants have not been built until recently, when China showed the wish to become more self-sufficient in energy.

As application of coal technology to biomass is not straightforward, several parties have engaged in the development of dedicated technology. In Austria, a 1 MW SNG pilot plant was built downstream the Fast Internally Circulating Fluidized-Bed (FICFB) gasifier in Güssing (www.ficfb.at), using fluidized-bed methanation technology from PSI in Switzerland [5]. In Sweden, Göteborg Energi plans to start a 20 MW plant in 2012, using the same type of gasifier but different methanation technology (www.goteborgenergi.se). If successful, a 200 MW plant will follow. In the Netherlands, ECN is developing the MILENA gasifier which uses less steam and can obtain a higher efficiency than the FICBF gasifier [6]. Construction of a 10 MW pilot plant is planned to start in 2012.

Both the FICFB and MILENA gasifier can produce virtually N₂-free gas without the need for an air separation plant. At present, the producer gas needs to be

compressed for conversion into SNG. That step can be deleted if the gasifiers are further developed to operate at higher pressure.

High-pressure biomass gasification has already been demonstrated in Värnamo, using an air-blown Circulating Fluidized-Bed (CFB) gasifier. Conversion of that gasifier for operation on O₂ and steam has been delayed by lack of funding (<http://lnu.se/research-groups/chrisgas/project-objectives?l=en>).

Co-gasification of coal and biomass at high temperature and pressure in an Entrained Flow (EF) gasifier is used to reduce the CO₂ impact of the Buggenum coal power plant in the Netherlands (<http://www.nuon.com/company/core-business/energy-generation/power-stations/buggenum/>). Ongoing research aims to increase the biomass share in the fuel to 50%, but operation without coal requires a different concept. Anyhow, the high temperature produces syngas which makes the process more suitable for the production of chemicals and liquid fuels than SNG.

3. Problem definition

As mentioned in the Introduction, SNG production from producer gas can be more efficient because of the hydrocarbon content. Hydrogenation of hydrocarbons with 2 or more C-atoms to methane is less exothermal than the reaction of CO with H₂ to methane. The effect is made clear by Table 1, which shows the composition (on dry basis) of MILENA producer gas by volume and energy content, and the energy efficiency of conversion to methane. The non-methane hydrocarbons contribute one third of the heating value of the producer gas. Other medium-temperature gasifiers may produce less tar and hydrocarbons, but the overall picture is similar.

Component	Vol. % dry	Energy %	Eff. % =>CH ₄
CO + H ₂	60	40	77
CH ₄	13	27	100
C ₂ H ₂	0.3	1	81
C ₂ H ₄	4.2	14	89
C ₂ H ₆	0.3	1	96
C ₃ H ₆	0.1	0.5	90
C ₆ H ₆	1.0	8	90
C ₇ H ₈	0.1	1	91
Tar	0.5	7	91

Tab. 1: Combustible components in MILENA producer gas and energy efficiency of conversion to methane.

The contribution of tar to the producer gas heating value is considerable, but so are the technical challenges. Given the effort spent on tar removal for simpler applications, it is not realistic to suggest tar conversion into methane. Tar has to be removed from producer gas. The OLGA technology, developed by ECN and sold by Dahlman (www.dahlman.nl), removes completely all but the most volatile tar compounds [3]. Removed tar can be used to cover the gasifier heat demand or supply process heat.

The other non-methane hydrocarbons account for 25 to 30% of the energy content of producer gas. The unsaturated and aromatic ones are notorious for their tendency to form carbon deposits (soot or gum) on nickel methanation catalysts. Acetylene may be the worst example, but benzene and ethylene behave similarly and are present in larger amounts. That's why this article focuses on them as a nuisance, at least to begin with.

4. Problem solutions

Solutions to the problems caused by benzene and ethylene are basically simple: remove the unwanted compounds

or create conditions which prevent the formation of carbon deposits.

The second option sounds most attractive, given the compounds' important contributions to the gas heating value. The main factors determining the fate of benzene and ethylene are the relative amount of H₂ and/or steam and the temperature. Adding H₂ may be an option to store temporary excess electricity from renewable sources, but otherwise steam will have to be used. Research at ECN on the effect of steam addition makes clear that finding the right conditions is not straightforward. Even if steam can solve the carbon problem, heat use for steam production will reduce the system efficiency.

The PSI fluidized-bed methanation technology may offer a more attractive solution, by creating conditions for re-gasification of carbon deposits within part of the bed [7]. Whether that technology can handle the amount of benzene given in Table 1 still remains to be seen, as benzene was almost completely removed upstream of the methanation section in the Güssing pilot SNG plant.

The other option to solve the carbon problem, removal of the troublesome components, poses two questions: how to remove them, and how to dispose of them?

In the Güssing pilot SNG plant, benzene and remaining tar compounds are removed by an RME scrubber working at 5°C. In the Great Plains Synfuels plant, benzene and other volatile tar compounds are removed by scrubbing at -40°C with methanol in the Rectisol gas cleaning unit. Actually, benzene capture is a side effect of the process designed to remove sulphur compounds and CO₂. Benzene and other organic vapours can also be adsorbed on active carbon. Impregnated forms of active carbon can be used to capture sulphur compounds as well.

Each of these three techniques allows recovery of captured organic compounds from the working fluid or solid by distillation or steam stripping. As none of them is specific for benzene, the product obtained is a mixture which depends on the gasifier and upstream gas cleaning.

In Güssing, the mixture is simply used as fuel in the combustion part of the FICFB gasifier. There, it covers heat demand which otherwise is met by burning part of the producer gas. Effectively, more producer gas becomes available for the methanation step.

The lower heat demand of the MILENA gasifier does not allow that solution. Neither does a CFB gasifier, where the recycled mixture could only compete with biomass char or tar for the limited amount of oxygen available. Still, the recycled mixture could be used to generate process steam, or to cover heat demand elsewhere or at times when the gasifier is out of operation. The latter approach is used for tar at the Harboøre biomass CHP plant (www.volund.dk). If there is no reasonable direct use of the benzene mixture as fuel, reforming with steam to syngas in a dedicated reactor can be considered. The syngas can be added to the producer gas for conversion into methane.

It should be realized, however, that the benzene mixture contains organic sulphur compounds. If the mixture is burned in the gasifier, it will just add to the sulphur emissions from biomass char and have to be treated likewise. If the mixture is used separately, it requires an installation able to handle sulphur containing fuel. If the mixture is to be reformed to syngas, sulphur will have to be removed before the methanation catalyst.

If only benzene and light tar compounds are removed, C₂-compounds still have to be taken care of. Research at ECN shows that acetylene and ethylene can be made to react with H₂ present in producer gas.

Noble metal catalysts can promote hydrogenation to C₂H₆ at about 200°C. HDS catalysts can also do the job, but require higher temperature. HDS catalysts simultaneously promote H₂ production by water-gas shift and conversion of organic sulphur and nitrogen compounds. Unfortunately, the catalyst volume required for operation at atmospheric pressure is too large for practical purposes. The effect of higher pressure is under investigation.

If complete removal of all troublesome components is required, cryogenic separation may be the answer. Energy consumption is significant, but products with 99% purity can be obtained.

5. Process evaluation

Whether separation processes can be economical depends on the value and amount of products that can be obtained and on the evaded costs. Table 2 shows the expected product yield for 7000 hours/year operation of a 50 MW biomass input MILENA gasifier. The amounts of benzene, toluene and xylene have been calculated assuming 10%, 30% and 80% capture by the OLGA tar removal.

Component	Amount tonne/year
C ₂ H ₂	200
C ₂ H ₄	3400
C ₆ H ₆	2200
C ₇ H ₈	250
C ₈ H ₁₀	10

Tab. 2: Expected yearly product yield of a 50 MW MILENA gasifier.

Market prices of unsaturated and aromatic hydrocarbons are strongly linked to the crude oil price. At the end of 2010, prices were close to 20 €/GJ (~700 €/tonne for C₆H₆, C₇H₈ and C₈H₁₀, and ~1000 €/tonne

for C₂H₄) when the crude oil price was about 10 €/GJ (90 \$/bbl). Acetylene may be even more valuable, but information on its bulk price is more difficult to obtain.

Until a few years ago, natural gas was about 30% cheaper than oil on energy basis. Now, the difference is even larger, making SNG production from ethylene and benzene seem to be a waste of money. For the moment, however, economics are governed by the subsidy or other support schemes which do exist for bio-SNG but not yet for bio-chemicals. Moreover, the market is not yet ready to accept small streams of limited purity. That situation may change if more and larger bio-SNG plants are realized.

Separation of awkward hydrocarbons from producer gas can increase the useful life of the methanation catalyst. The use of noble-metal or HDS catalysts may also solve (part of) the problem. In the balance of cost and profit, combination with other gas cleaning steps, like the removal of sulphur compounds and CO₂, may be the deciding factor. The optimum solution will depend on the plant scale, local conditions and market development.

6. Conclusion and Outlook

Gasification of biomass at moderate temperatures promises the highest efficiency for bio-SNG production, but produces unsaturated and aromatic hydrocarbons which easily form carbon deposits on methanation catalysts. Steam and H₂ addition may suppress carbon formation, but reduce the system efficiency. Removal of the responsible compounds, followed by reforming or use, seems a promising alternative. The optimum solution will depend on the gasifier type and plant size.

For small-scale bio-SNG plants, use as fuel is the obvious choice, provided there

is sufficient heat demand. The alternative is reforming to syngas in a dedicated reactor, followed by conversion to methane.

For large-scale bio-SNG plants, or even for medium-sized ones in a more mature market, the nuisance compounds may become money makers. A quick inventory shows that the market value of the compounds can easily be two to three times the value of the SNG energy equivalent.

The history of the Great Plains Synfuels plant proves how the product portfolio can develop [8]. It now includes aromatic and phenolic hydrocarbons like discussed above, CO₂, ammonia and sulphur from the producer gas cleaning, and even krypton and xenon from the air separation unit. The plant now uses part of the syngas to produce ammonia instead of SNG. In 2008, the coproducts accounted for 44% of the total revenues www.dakotagas.com/Products/index.html. It may have taken decades to reach that point, but it proves that polygeneration can be a viable option.

7. Acknowledgements

The work reported was performed with financial support from the Dutch Ministry of Economic Affairs, Agriculture and Innovation and from the Energy Delta Gas Research (EDGaR) program.

8. References

- [1] L.W.M. Beurskens and M. Hekkenberg, report ECN-E--10-069 (2011).
- [2] C.M. van der Meijden et al., Biomass and Bioenergy **34** (2010) p302.
- [3] L.P.L.M. Rabou et al., Energy and Fuels **23** (2009) p6189.
- [4] S. Anis and Z.A. Zainal, Ren. Sust. Energy Rev. **15** (2011) p2355.

[5] J. Kopyscinski et al., Fuel **89** (2010) p1763.

[6] A. van der Drift et al., Proc. 18th European Biomass Conference & Exhibition (2010) p1677.

[7] M.C. Seemann et al., Appl. Cat. A **313** (2006) p14.

[8] G. Baker et al., Proc. 7th Int. Pittsburgh Coal Conf. (1990) p.561.



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Annex

Benzene and ethylene in bio-SNG production: nuisance, fuel or valuable products?

Luc Rabou & Bram van der Drift



Bio-SNG \equiv CH₄ from biomass via gasification

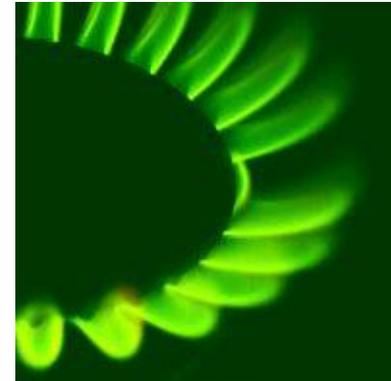
Biomass

=>

“Green” gas



=>



Biomass “chemistry”

Biomass is almost exactly **hydro-carbon** = carbon + water



More exactly:



$$n = 2.7$$

~25% moisture

$$n = 6.7$$

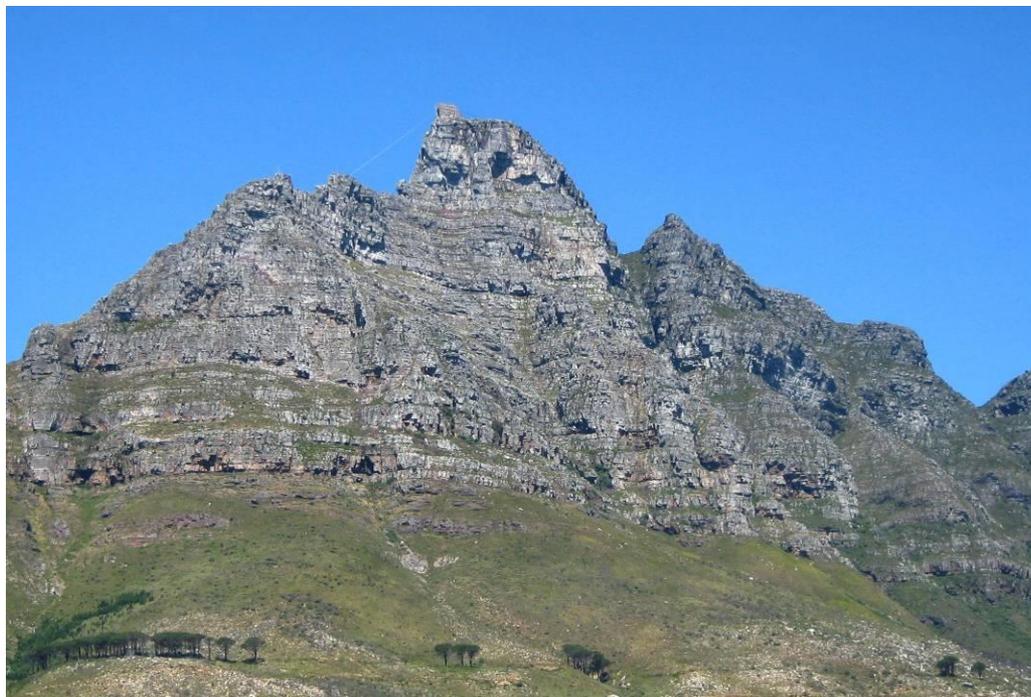
~45% moisture

Biomass conversion to SNG

In theory, biomass with 25% moisture could be decomposed to:

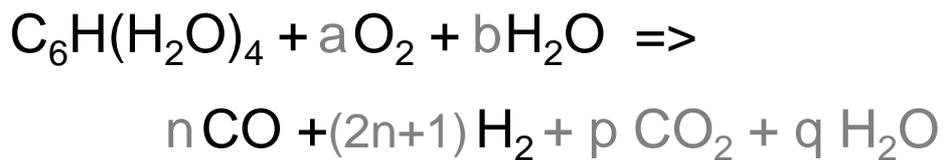


In practice:

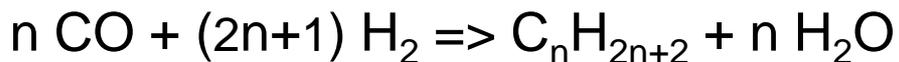


How to get over the mountain (1)

The “easy” way over the top:

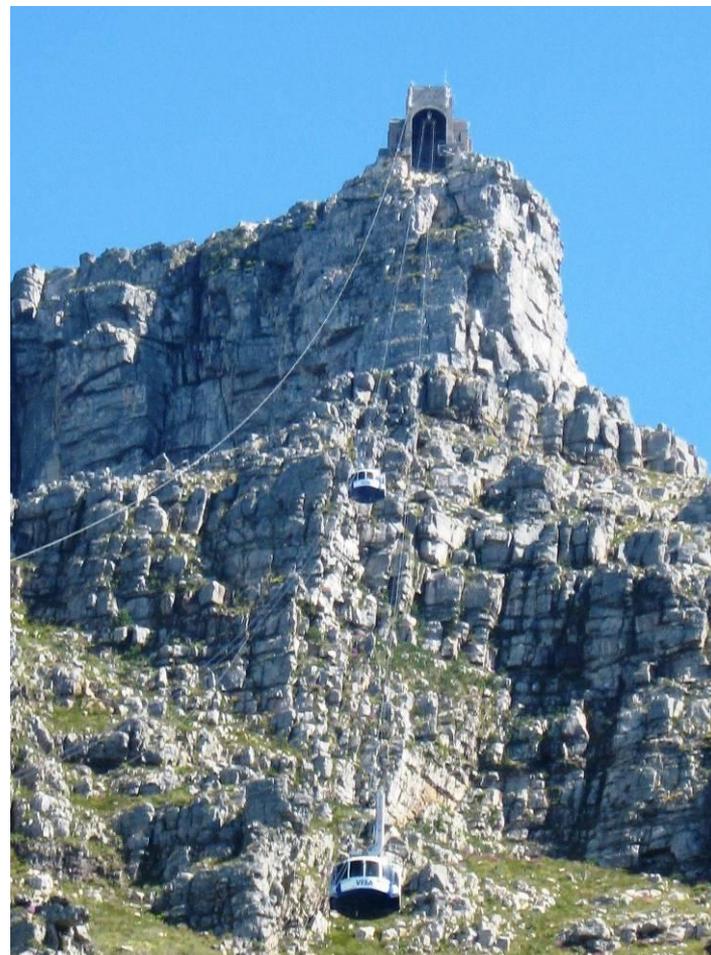


followed by:



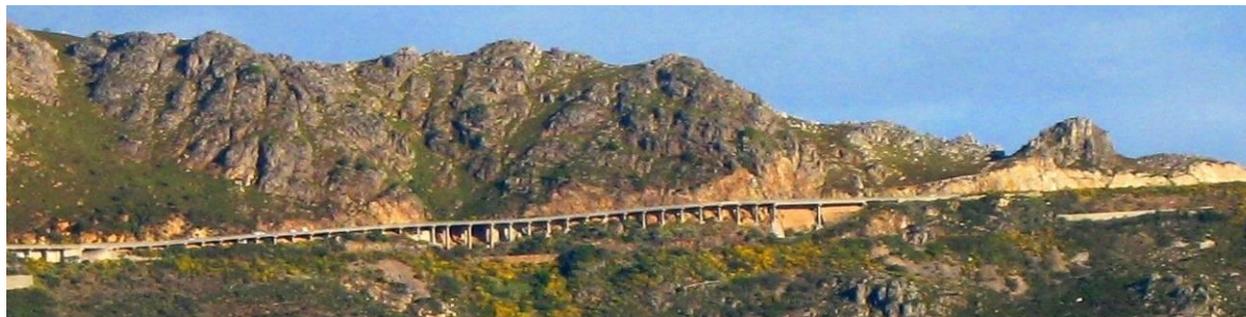
$n = 1$ for methane,

$n \geq 1$ for Fischer-Tropsch

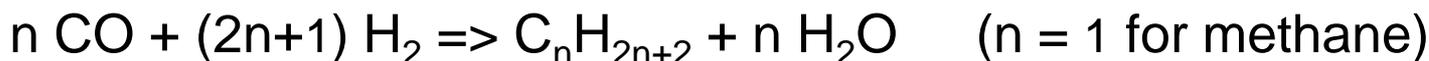


How to get over the mountain (2)

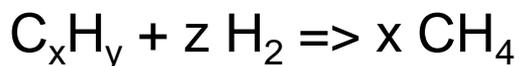
The “long way over the pass”:



followed by:



and



How to get over the mountain (3)

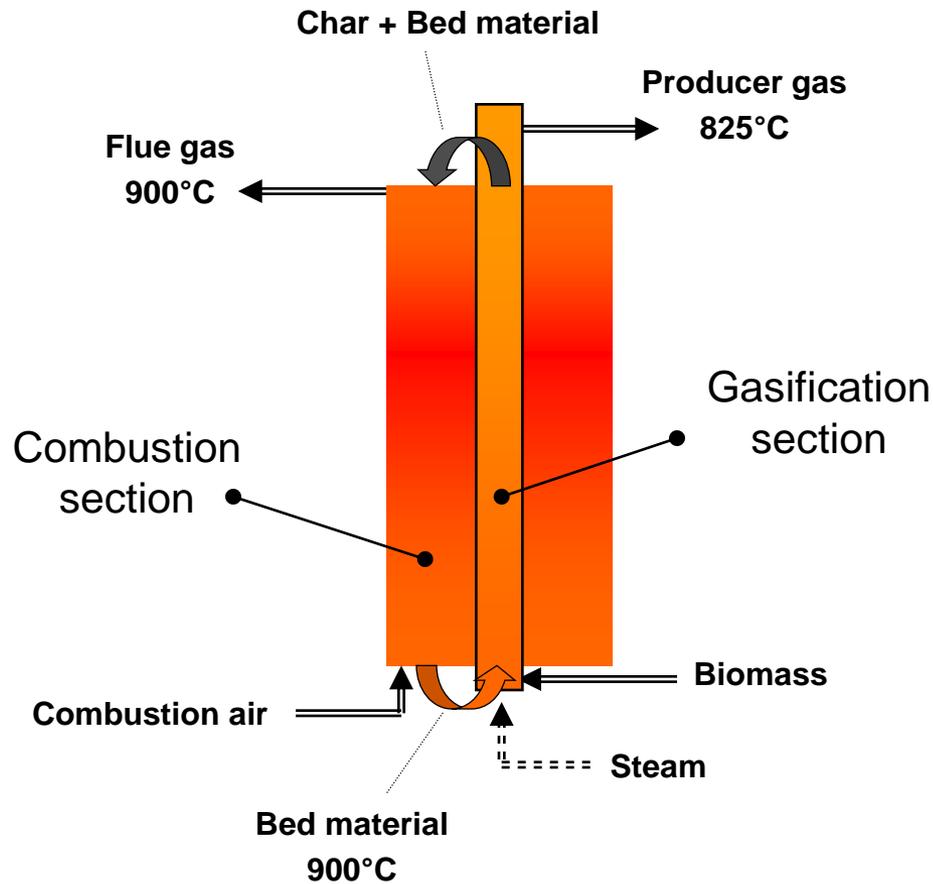
Either way:



e.g.

- Biomass feeding
- Biomass ash
- Gaseous compounds of S, Cl, N and trace elements
- Tar

Our choice: MILENA indirect gasifier



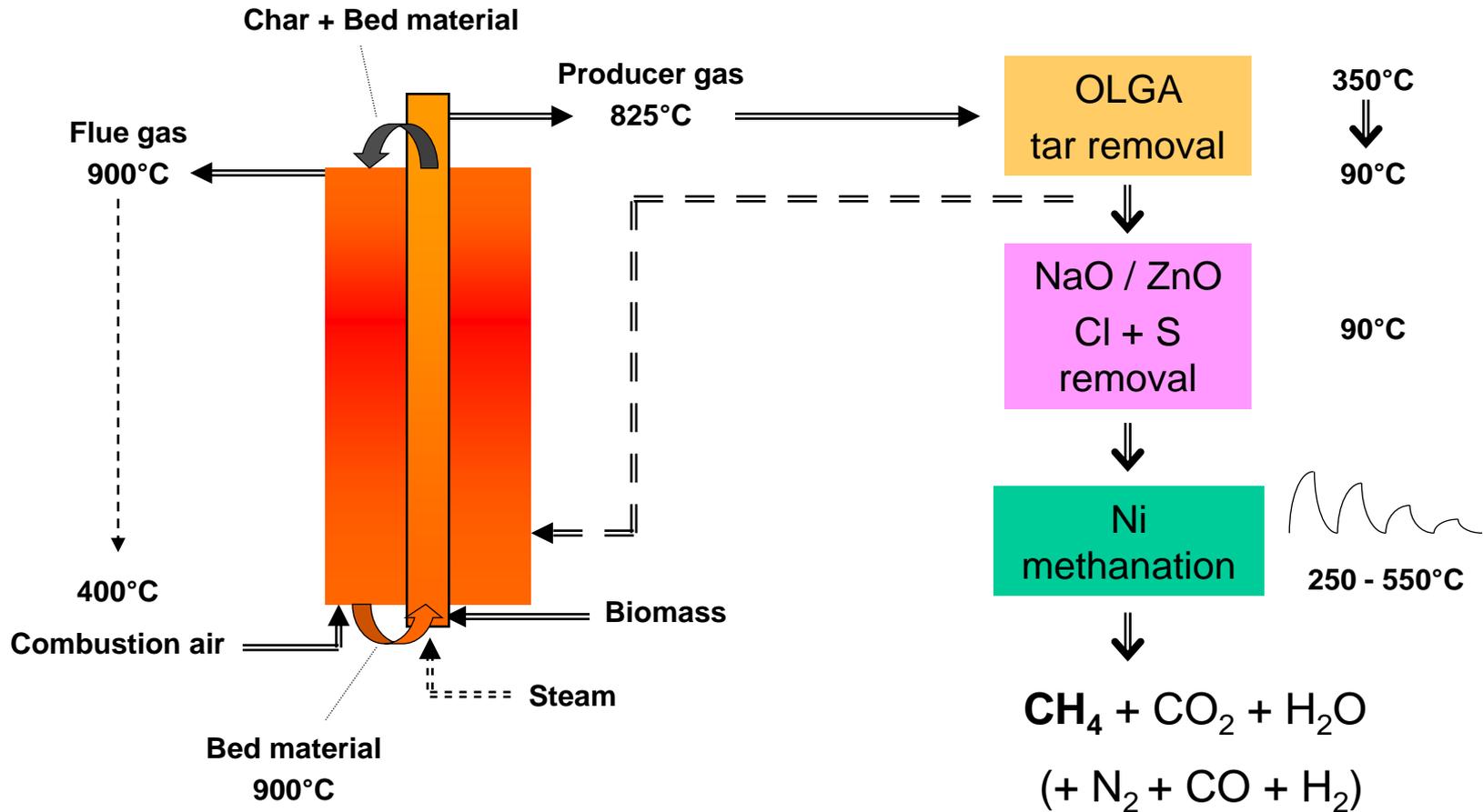
MILENA producer gas

Component	Vol % (dry)	Energy %	Efficiency [‡] %
CO + H ₂	60	40	77
CH ₄	13	27	100
C ₂ H ₂	0.3	1	81
C ₂ H ₄	4.2	14	89
C ₂ H ₆	0.3	1	96
C ₃ H ₆	0.1	0.5	90
C ₆ H ₆	1.0	8	90
C ₇ H ₈	0.1	1	91
Tar	0.3	6	91
CO ₂ + N ₂	20		

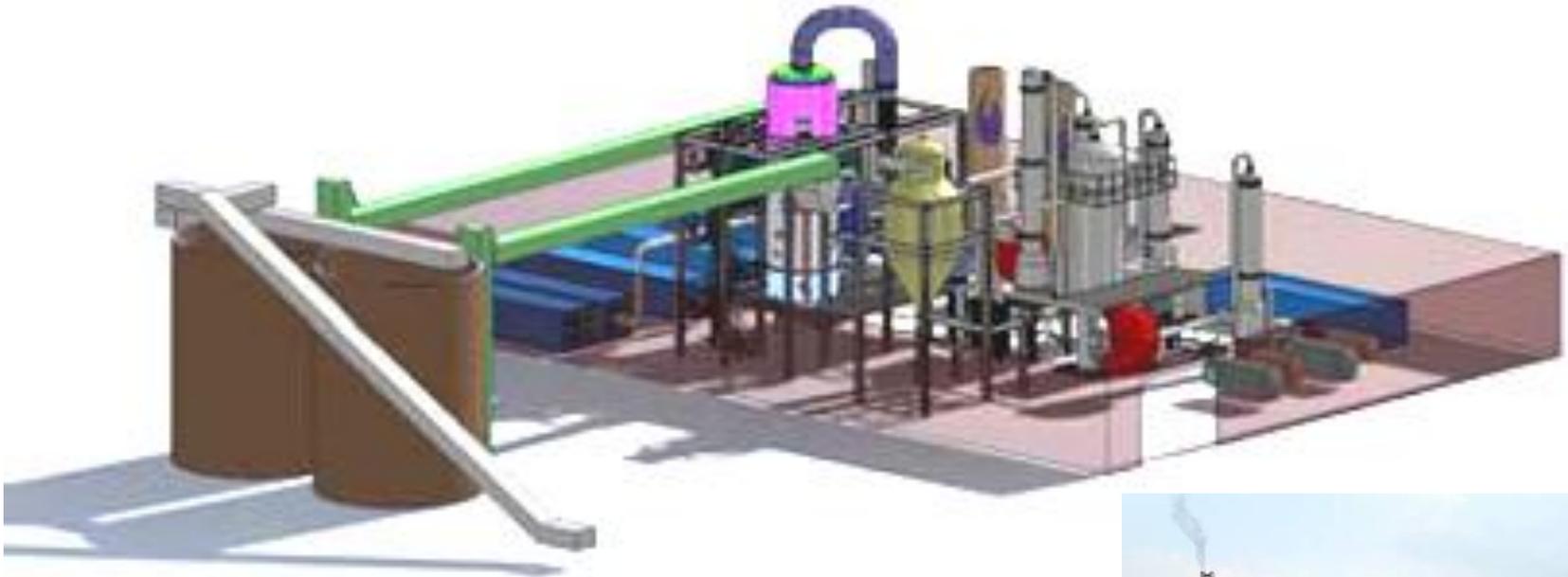
[‡] X + H₂ => CH₄

C₂H₂ + C₂H₄ + C₃H₆ + C₆H₆ + C₇H₈ ≡ ± 25% of producer gas heating value

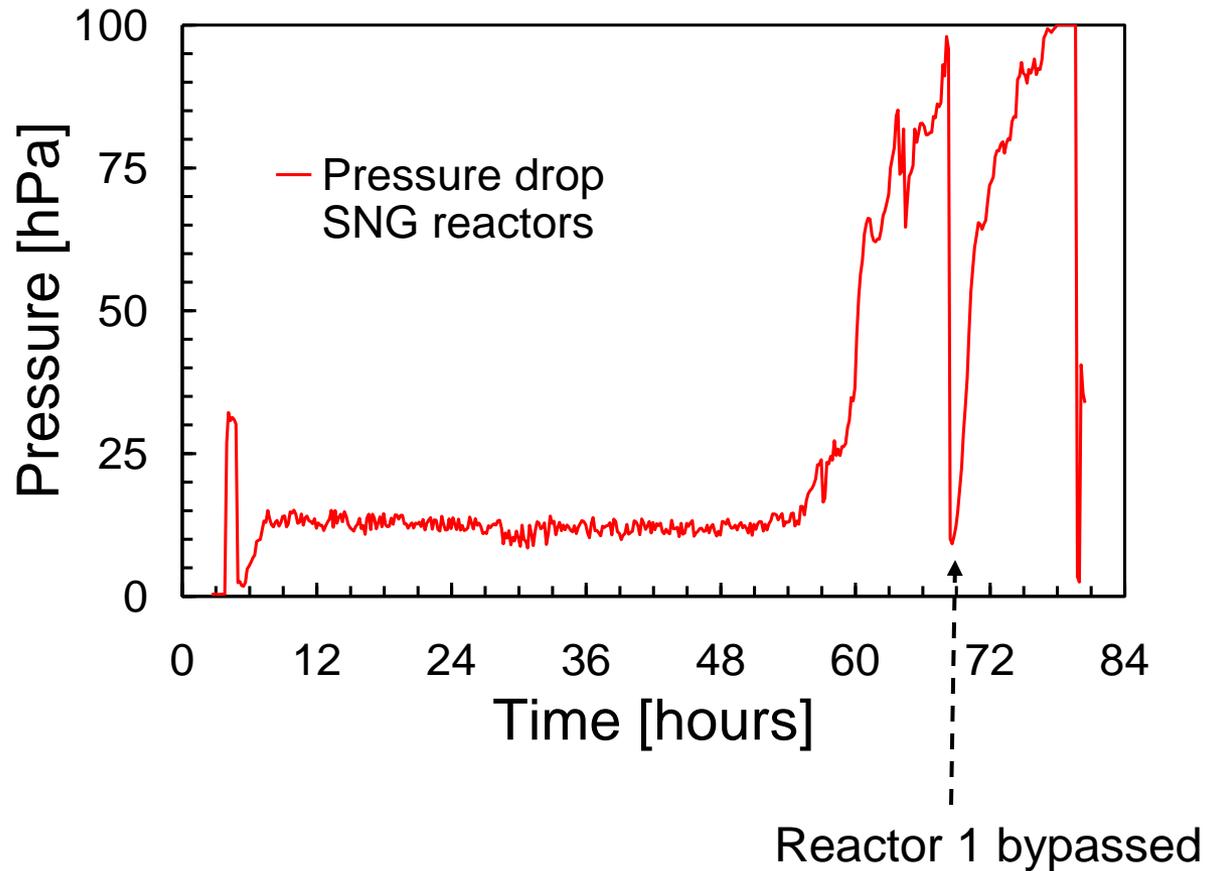
SNG using MILENA indirect gasifier



Preliminary design for 12 MW plant



Early result (2006)



Ni catalyst blocked by carbon dust

Problem analysis

Carbon formation probably caused by:

unsaturated and aromatic hydrocarbons in producer gas

ethylene, acetylene, propene

C₂H₄, C₂H₂, C₃H₆

benzene, toluene, xylene

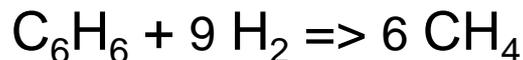
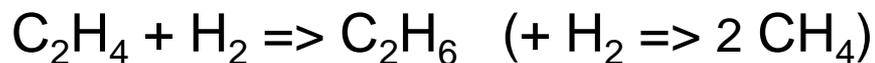
C₆H₆, C₇H₈, C₈H₁₀

$C_2H_2 + C_2H_4 + C_3H_6 + C_6H_6 + C_7H_8 \equiv \pm 25\%$ of producer gas heating value

=> Removal would reduce SNG output considerably

Options

Hydrogenation:



Reforming:

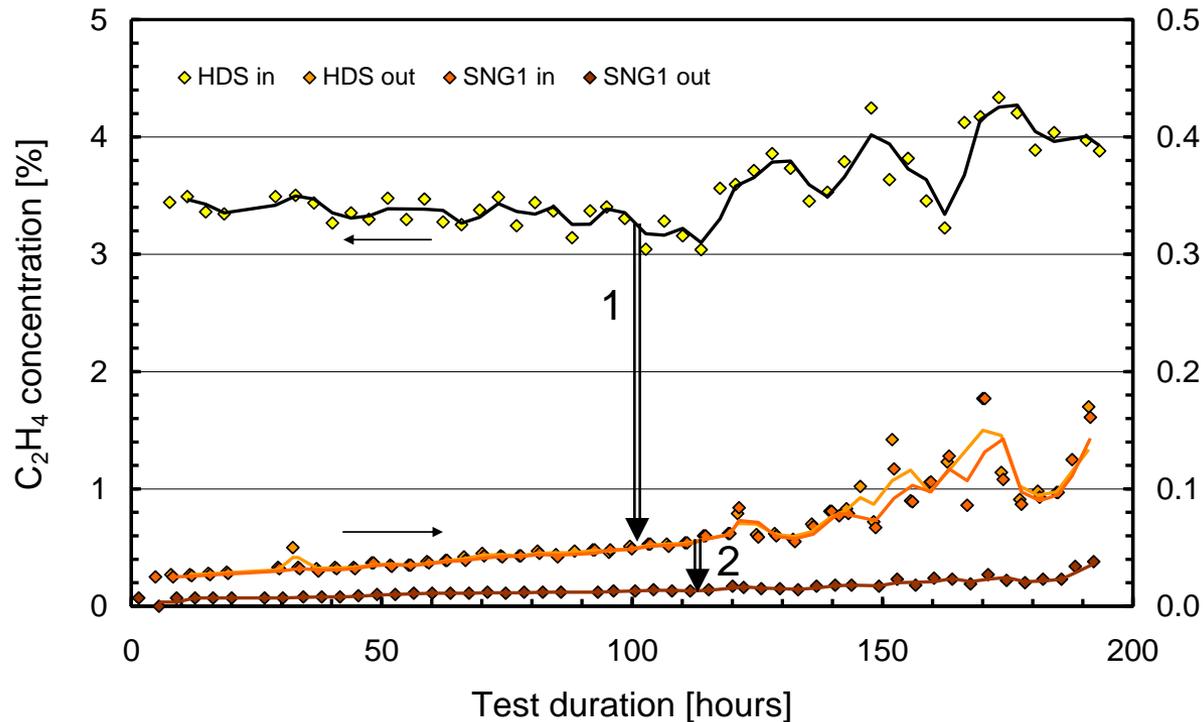


- In producer gas, with H_2 and H_2O present or added
- In dedicated reactor, after separation, with added H_2 and H_2O

Ethylene conversion in producer gas

Test lay-out:

HDS CoMoS	H ₂ S-removal ZnO	Hydrogenation SNG1 (NM1)	Reforming SNG2 (NM2)	Methanation SNG3 (Ni)
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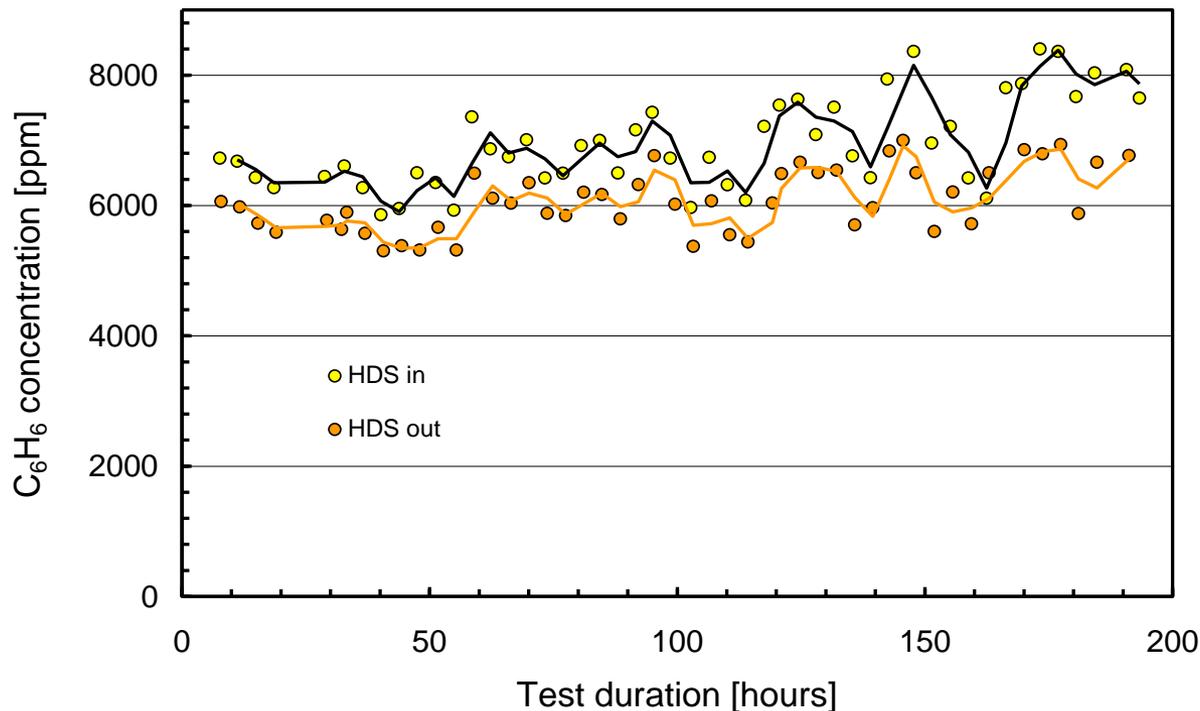


- 1 Hydrogenation to C₂H₆ and CH₄ by HDS catalyst
- 2 Hydrogenation by noble-metal catalyst

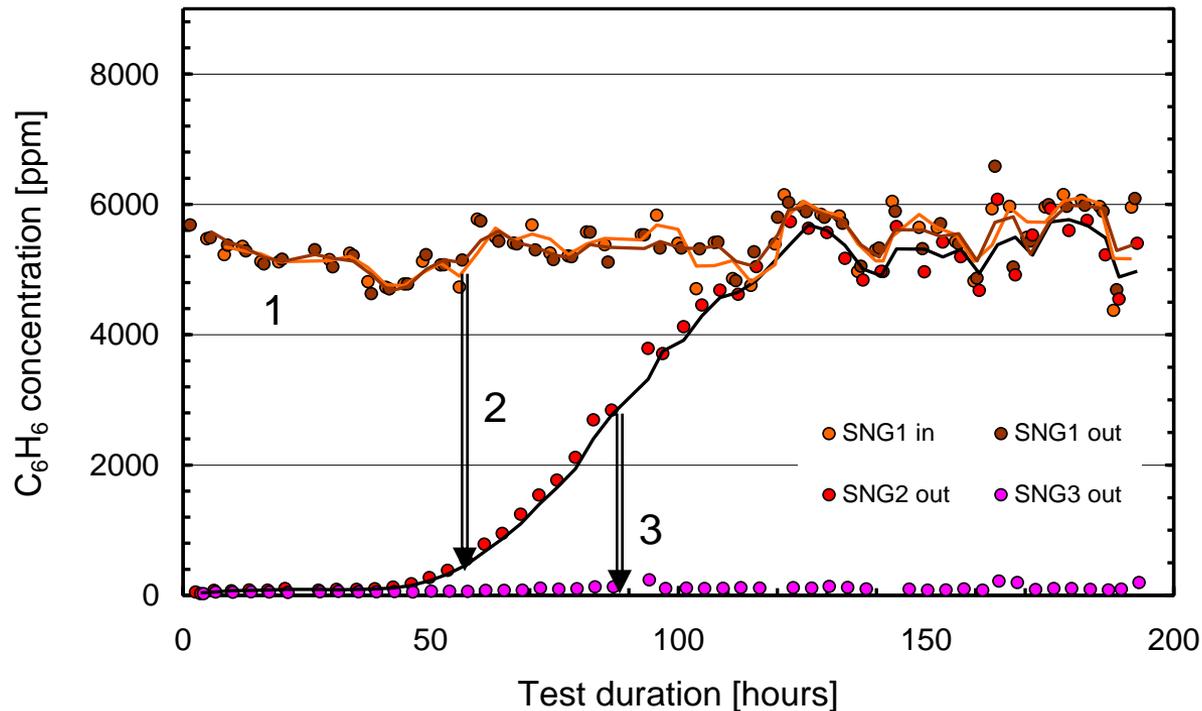
Main effect of HDS catalyst

Hydrogenation of C_2H_x and CO / H_2 shift \Rightarrow temperature rise

No effect on benzene (only dilution by increased dry gas volume)



Benzene conversion in producer gas

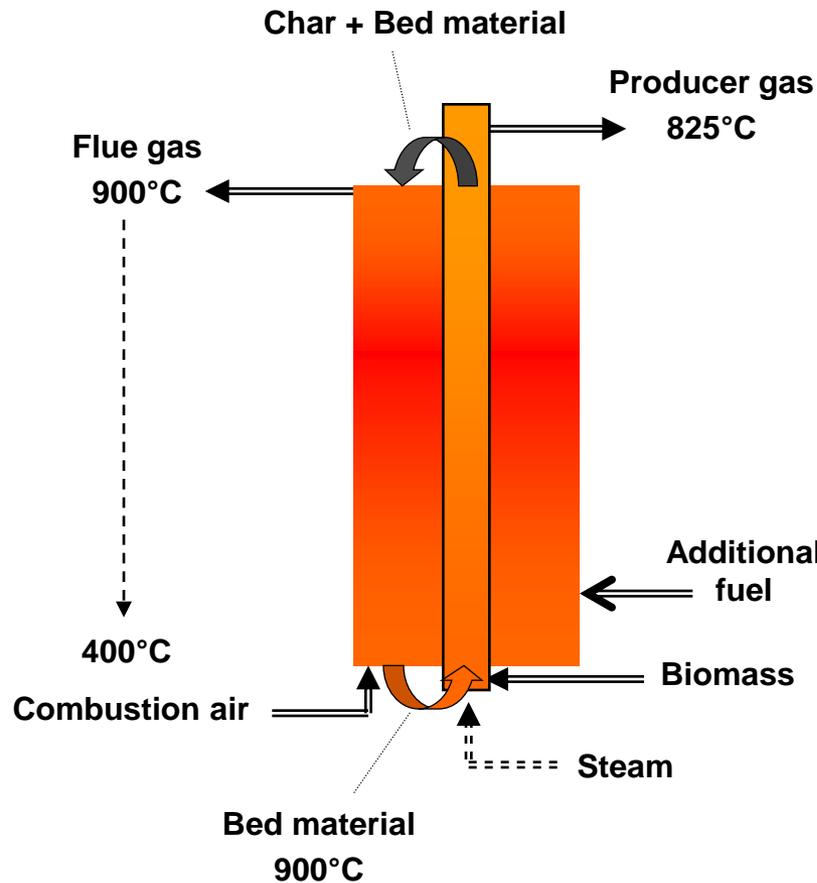


- 1 No effect of noble-metal hydrogenation catalyst
- 2 Conversion by noble-metal reforming catalyst
- 3 Conversion by Ni methanation catalyst (with C-formation)

Provisional conclusions

- Ethylene hydrogenation achievable
 - Benzene conversion complex
 - Expensive additional catalysts required
 - Separation from producer gas may be needed
 - After separation, alternatives may be more attractive
 1. Fuel
2. Product
- 10 – 25% of producer gas heating value

Additional fuel in MILENA: heat balance



Gasifier IN / OUT

Biomass LHV	100
Steam	1
Bed material (net)	15
Producer gas LHV	- 85
Gas latent heat	- 14
Char LHV	- 17

Combustor IN / OUT

Char LHV	17
Tar LHV	6
Air latent heat	4
Bed material (net)	- 15
Flue gas latent heat	- 11
Heat loss	- 1

Fuel for heat & power

- Fuel use for district heating

For Dutch consumers:

heat price + distribution costs \equiv natural gas price + distribution costs

=> heat value can be as low as 1/3rd of gas price

- Co-generation, fuel for back-up heat delivery => flexibility
- Co-generation, fuel for steam production => electricity

Value = price of equivalent replacement fuel

Product (“green” chemicals)

- Ethylene and benzene are important chemicals
- Chemicals more valuable than crude oil
 - => certainly more valuable than natural gas
- Products may not be pure
 - ethylene mixed with acetylene and ethane
 - benzene mixed with toluene and xylene
- Products may be contaminated
 - benzene mixed with thiophene

Expected yield for 50 MW MILENA

50 MW \equiv 100 ktonne/year biomass input

Component	Yield (tonne/year)	Production NL (tonne/year)
C_2H_2	200	
C_2H_4	3,400	~2,000,000
C_2H_6	200	
C_6H_6	2,200	~1,000,000
C_7H_8	250	
C_8H_{10}	10	

Substantial amounts, but can they be sold?

The big example

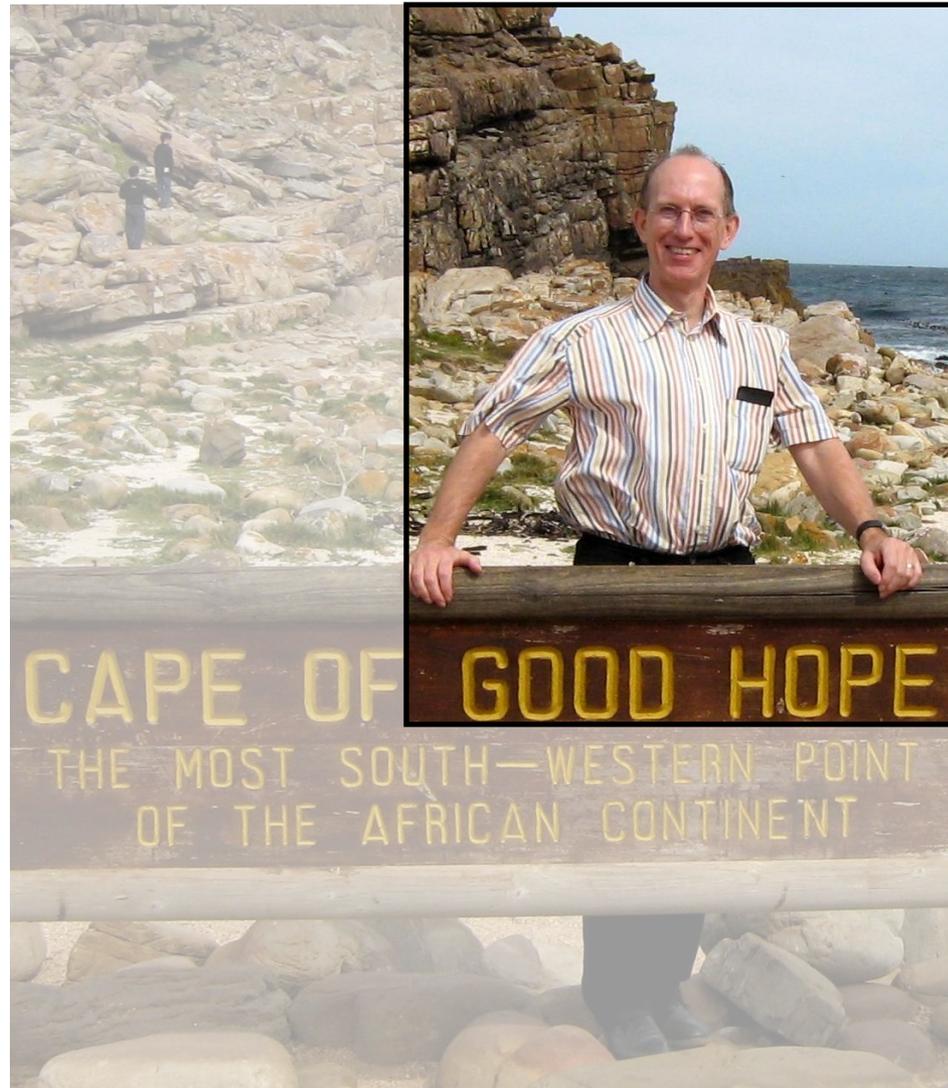


In 2008, co-products accounted for 44% of the total revenues
(but represented only 13% of the fuel energy input)

Conclusions

- Ethylene and benzene hinder SNG production
- Hydrogenation or reforming can solve problems
- Benzene most difficult compound to handle
- Co-generation or co-production can be more profitable than just SNG production (without subsidies)
- Nuisance compounds can become moneymakers
- Scale matters

Summary



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