Co-production schemes in biomass gasification

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Co-production schemes in biomass gasification

Vladan Krzelj
September, 2014
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Summary

ECN is developing a technology for the production of Substitute Natural Gas (SNG) from biomass. In the producer gas ethylene and benzene make only a small part of the total volume (about 5 mol %) but, on the other hand, they make a large part of the energy content. However, both of these molecules have a higher economic value than SNG. Additionally, they are known coking precursors for methanation catalysts. Therefore, separating them from the producer gas may “kill two birds with one stone”.

The goal of this project is to describe and experimentally validate promising ways to separate valuable co-products in the MILENA-OLGA to bioSNG system.

Based on differences in chemical and physical properties of benzene and ethylene, compared to the rest of the components in the producer gas, long list of option has been created in order to achieve project objectives. Subsequently, it was reduced to four options: ethylbenzene production, aromatization of ethylene, hydroformylation of ethylene and cryogenic separation.

Ethylbenzene production and aromatization of ethylene were selected as the most promising ones from the combination of added value and expected limited increase in capital and operating costs. Additionally, they were considered to be most easily integrated into the current biomass to bioSNG system. Both of those options are regarded as reactive separation techniques.

The experiments were planned and performed in order to prove the concept of reactive separation technique. Ethylene conversion of 95% was achieved. It has been shown, that 40% of ethylene is converted to aromatics. Additionally, influence of temperature, addition of benzene and catalyst acidity has been tested. It has been shown, that distribution between aromatics can be influenced with temperature and benzene addition.
Based on the insight obtained from experimental results, coupled with knowledge gained from literature study and following the principles of process synthesis, two new co-production schemes in Biomass to bioSNG were created:

- Ethylene benzene production process scheme (EB case)
- Diluted ethylene aromatization process scheme (DEA case)

The proposed schemes were modelled in AspenPlus. The outputs from these simulations were used for economic assessment of co-production schemes compared to reference case.

The economic benefits of co-producing chemicals in a 100MW plant of biomass thermal input have been quantified. It has been shown that proposed co-production schemes are reducing production costs of SNG.

Finally, ethylbenzene production has been identified as the most promising one offering up to $5/GJ savings in production costs of SNG.
Biomass is anything made from living or recently dead plant or animal material. For thousands of years humans have harnessed natural sources of energy, such as wind power for sailing ships and windmills, and water power from fast-flowing rivers. We have also learned how to exploit biomass for fuel and even today many societies still depend on wood, peat and even cow dung for fuel. Dramatic change came with the discovery and use of fossil fuels, these being energy dense (giving lots of energy per mass of material) and easily transportable. It was coal that powered the Industrial Revolution and the invention of the steam engine that revolutionized transport. Oil then followed as an even more convenient and efficient fuel than coal, allowing humankind to draw on vast resources of power and so increase dramatically its consumption of energy. In the last few decades we have recognized two very stark and significant facts. First, the supply of these fuels is finite. Secondly, by burning these fossil fuels we are releasing vast quantities of carbon dioxide into the atmosphere, adding significantly to the greenhouse effect and its potentially catastrophic impact on sea levels, weather patterns and agriculture. So, a new revolution is required to provide alternative forms of energy which are both sustainable and kinder to the environment.

Three driving forces for the production of biofuels are:

- saving a valuable finite resource - fossil fuels which will become more expensive as they become scarcer
- climate change – the need to reduce the emissions of carbon dioxide
- energy security - countries with a shortage of crude oil and natural gas believe that they are vulnerable and want to develop their own fuel supplies.

First generation of biofuels was based on conventional agricultural commodity crops. This was a controversial issue because the increase in demand for conventional food feedstocks for biofuels is likely to exacerbating price volatility in the food market particularly the poor in developing countries. Therefore the scientific community is changing the focus from first generation biofuels to second generation biofuels, utilizing mainly lignocellulosic material. The main
types of first generation biofuel used commercially are biodiesel, ethanol and biogas while the second generation biofuels are bioethanol, Fisher-Tropsch biodiesel, Bio-DME and Bio-SNG. [1]

1.1 BioSNG

Natural gas is a convenient and environmentally friendly fuel used all over the world. It has a wide range of applications:

- Large scale electricity production in Combined Cycles
- Decentralized Combined Heat and Power production (CHP)
- Transportation, as a Compressed Natural Gas (CNG) or Liquefied Natural Gas (LNG)
- Chemical industry, as a feedstock for many chemicals

In the Netherlands natural gas represents 46% of the Dutch (primary) energy consumption. The main applications of natural gas are chemistry (7%), power production (23%), and – by far the largest application – the production of heat (70%), of which 40% is consumed by households\(^1\). However the production of natural gas in the Netherlands has reached its maximum and it will gradually decrease.

The substitution of natural gas by a renewable equivalent is an interesting option to reduce the use of fossil fuels and the accompanying greenhouse gas emissions, as well from the point of view of security of supply. In NL, the ambition has been expressed to replace 50% of the natural gas by Green Gas from biomass in 2050. Being a direct substitute of a natural gas, bioSNG can be injected directly into the gas grid taking the advantage of the existing structure. However, to be injected directly into the system, bioSNG needs to meet strict requirement regarding Wobbe index, gross calorific value, maximum liquid hydrocarbon content, water dew point, total sulphur content etc.

There are two main options to produce SNG from biomass. It can be done either with anaerobic digestion (biological conversion at low temperature) or with gasification (thermochemical conversion at high temperature). Gasification belongs to the second generation of Bio-SNG production process and has more potential because of the large scale and the ability to use biomass/waste that does not interfere with food.

---

\(^1\) Statistics Netherlands (CBS), 2006 ([www.cbs.nl](http://www.cbs.nl))
Background

ECN has put lot of effort into development of technology for the production of Substitute Natural Gas (SNG) from biomass. MILENA indirect gasification and OLGA tar removal are the first steps of the process. These technologies and other units of the process are described in Appendix A.2. The current process scheme is shown in the Figure 1.

![Figure 1: Current process scheme Biomass to bioSNG](image)

The typical gas composition after tar removal, on dry basis, is given in the Figure 2. Ethylene and benzene make only a small part of the total volume in the producer gas (about 5 mol %). On the other hand, as it can be seen from the Figure 2, they make a large part of the energy content. Both of these molecules are known coking precursors in the methanation section. In the current system, MILENA-OLGA to SNG, ethylene is being hydrogenated in the HDS reactor, and benzene is being reformed in the reformer. On the other hand, both benzene and ethylene have much higher economic value than SNG.

![Figure 2: Typical gas composition after OLGA, dry basis; Share in gas heating value, after OLGA](image)
2.1 Project objective

The goal of this project is to describe and experimentally validate promising ways to separate valuable co-products in the MILENA-OLGA to bioSNG system. The final objective is to quantify the possible benefits of co-production of chemicals in a biomass to SNG system.

The main deliverables of this project are the following:

- Identifying the options from the technical and economical perspective to separate benzene and ethylene in the MILENA-OLGA to bio-SNG system.
- Selecting options and designing process scheme for overall process in the Aspen Plus software package for the 100MW plant of biomass input
- Designing and performing the experiments for validation of the important assumptions
- Quantifying the economic benefits of co-producing chemicals in a 100 MW bioSNG plant.

2.2 Approach

The approach considered for reaching the project objectives was to find the appropriate difference in the physical or chemical properties in order to separate ethylene and benzene from the producer gas.

2.3 Identifying the options

Due to the low partial pressure of benzene and relative high boiling point, compared to the rest of the components present in the producer gas, absorption would be a reasonable method for the separation of benzene. The research about benzene, toluene and xylene (BTX) removal via scrubbing oils is currently being performed within ECN. The first results are quite encouraging. High level of benzene separation was achieved. [2] The technology is explained in more details in Appendix A.2.7.

The separation of ethylene from the producer gas stream proves to be a more difficult task than separation of benzene. Two different routes were considered for that purpose. The first is by exploiting the differences in the physical properties such as boiling point, solubility, molecular size, etc. Several options were considered: cryogenic distillation, membrane separation, absorption with organic solvents and adsorption on molecular sieves. Difference in the boiling point was considered as the only physical property that can offer a sufficient level of separation of ethylene from the producer gas. Therefore, cryogenic
separation was considered as the only option which utilizes differences in the physical properties.

The second route is by utilizing the chemical properties of ethylene; it’s reactivity of the “π” bond. This approach is known as reactive separation. The idea of this technique is to transform ethylene to products that are easier to separate and bring additional economic value. The various reaction paths of ethylene in chemical industry were studied in order to select possible reactions that can be used within reactive separation method [3]. The long list of possible reactions was created which was narrowed down eventually to three selections. The options that were chosen, based on reactive separation approach and studied in more details are:

- Alkylation of benzene (production of ethylbenzene),
- Aromatization of ethylene (mixed aromatics as a product)
- Hydroformylation of ethylene (propionaldehyde as a product)

These options will be discussed in the following subchapters.

2.3.1 Alkylation of benzene (Ethylbenzene as a product)

Ethylbenzene is produced on a large scale by combining benzene and ethylene in an acid-catalyzed chemical reaction shown in the Figure 3.

![Figure 3: Alkylation of Benzene](image)

Nearly all ethylbenzene produced in the world is used in the manufacture of styrene; therefore, ethylbenzene demand is determined primarily by styrene production. Consumption of ethylbenzene for uses other than the production of styrene is estimated to be less than 1%. Current worldwide consumption of ethylbenzene is 35 million tonnes. It is interesting to mention that manufacturers of ethylbenzene are the major buyers of benzene, claiming more than half of total output[2].

Until 1980 aluminium chloride was used in almost all of the ethylbenzene production facility as a catalyst (Friedel-Crafts process). Process dealt with problems of corrosion and waste disposal. In 1980 first commercial facility using a zeolite catalyst in vapour phase system started production (Mobil-Badger process) which was environmentally friendly alternative to previous process. Afterwards, liquid phase alkylation process were introduced which reduced required benzene to ethylene ratio and decreased xylene production (Lummus/UOP EBOne process) [4]. Liquid phase alkylation is not possible in our system because of the excess of gases in the system (see Figure 2).[3]

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2 [www.essentialchemicalindustry.org](http://www.essentialchemicalindustry.org)

3 CO, CO₂, H₂, CH₄ are considered to be inert in the alkylation reactions
Typically, the reactor system in the vapour phase is comprised of the parallel fixed bed reactors. Usual operating temperatures are between 320-450°C and 10-30 bar. Benzene is used in excess because a consecutive reaction is occurring (ethylene is reacting with ethylbenzene producing diethyl-benzene). Choosing the right ratio between benzene and ethylene is an optimization between selectivity towards ethylbenzene and operating costs in the separation section. Another reason for using benzene in excess is the temperature control since reaction is quite exothermic. In our case ethylene is diluted so temperature control is not considered to be an issue, since inert gases are acting as heat sink. The catalysts used are zeolites which are noncorrosive and non-polluting. The zeolites are essentially silica – alumina, which is environmentally inert. Because no aqueous waste streams are produced by the process, the equipment for waste treatment and for catalyst recovery is eliminated.

Additionally, ethylbenzene is economically more valuable product than SNG and much easier to separate than ethylene. It can be obtained as high purity product by distillation. The boiling point of ethylbenzene is 136°C compared to -103°C for ethylene. Main cause for zeolite deactivation is formation of coke inside the pores. However, the activity can be fully restored after regeneration in the hot air stream [5]. Moreover, zeolite catalysts are considered quite resilient to sulphur poisoning. The fact that diluted ethylene from FCC crackers (12%) has been used in industry for ethylbenzene production makes this approach more reasonable.

However, a disadvantage is that the stoichiometric ratio for ethylbenzene reaction is not correct in the producer gas in MILENA-OLGA to Bio-SNG system (4-8 to 1 in favour to ethylene). This is not considered to be a “no go” situation since there are certain options to deal with this drawback. Different scenarios were created in order to cope up with this challenge:

- Acquiring additional benzene from an external source (petrochemical industry- which would mean that part of the products will not be bio-based chemicals)
- Obtaining additional benzene from other SNG plants (additional three plants if biomass is used as a feedstock)
- Adjusting ethylene to benzene ratio (possibility of using and developing TARA technology [6] or changing gasification conditions)
- Partial hydrogenation of Ethylene (also eliminates concerns about acetylene and propylene presence in the feed but diminishes amount of product and further decreases partial pressure of the reactants)

2.3.2 Aromatization of ethylene (mixed aromatics as products)

Oxidative coupling of methane (OCM) to ethane and ethylene has been widely investigated in the past years. One of the drawbacks of the OCM process is the very low concentration of ethylene in the product stream (about 5 mol%). Separation at that low concentration is not economical. In order to make OCM
process more feasible, conversion of diluted ethylene to much less volatile products, like aromatic hydrocarbons, has also been investigated. [7]. The challenges in OCM case, separation of diluted ethylene, are quite similar to our case.

The idea is to make aromatics from the diluted ethylene in the producer gas after OLGA and remove them subsequently with the BTX scrubber. The reactions of ethylene aromatization are using zeolites as catalyst. Usually zeolite ZSM-5 is used, due to his known low coking activity and shape selectivity. The conversion of ethylene into aromatics involves a complex sequence of oligomerization, isomerization, cracking and cyclization reactions that occur on Brønsted acid sites in the zeolites. Simplified reaction path is given in the Figure 4. Additionally it has been shown that impregnating ZSM-5 with gallium can increase selectivity to aromatics. [8]. The role of gallium is to promote dehydrogenation of the acid-catalysed oligomerization and cyclization products. [9]

Advantage of this approach is that can be easily integrated with BTX removal process scheme. Further advantage is that product distribution can be influenced by different temperature and space velocity. [9]

2.3.3 Hydroformylation of ethylene (Propionaldehyde as a product)

Hydroformylation is an important commercial process for the conversion of alkenes, carbon monoxide and hydrogen into aldehydes to be further used in the production of various chemicals. The industrial processes are based on homogeneous catalysis. Heterogeneous catalytic processes are currently in the state of development [10]. In the hydroformylation reaction, olefin, carbon monoxide, and hydrogen are reacting over a catalyst to produce an aldehyde which has one more carbon atom than the feed olefin as it shown in the following figure.
The aldehyde can be treated with hydrogen to form alcohol. In commercial operations, the hydrogenation step is usually performed immediately after the hydroformylation step in an integrated system. The commercial catalysts are Cobalt or Rhodium complexes. Propionaldehyde, propanol and propionic acid are important organic chemical raw materials. The total capacity of propionaldehyde in the world was around 260 000 t/year in 2003. The scheme proposed for the hydroformylation case implemented in the MILENA-OLGA to Bio-SNG would be based on LP OxoSM process with liquid recycle (DOW chemicals, commercial process for hydroformylation of propylene). (See Appendix A.1.1)

The main advantages for using hydroformylation as a reactive separation technique are that product has different physical properties than ethylene (boiling point and polarity) which makes separation easier. On the other hand, since hydroformylation is a homogeneous catalytic reaction separation of the catalyst is an issue. This problem can be surpassed by using ionic liquids as a solvent [11] or by developing a process based on a heterogeneous catalysis [10]. Unfortunately, these processes in the phase of development and they are not commercially available.

It is important to mention that Bio-SNG production is further diminished (syngas is being used in the hydroformylation reaction) but since propionaldehyde has a higher market value than natural gas this is considered as a benefit. Advantage of this process is that the catalyst used (Rhodium) is sulphur resistant. Nevertheless, it is quite expensive and since it is a homogenous catalysis loss of catalyst is needed to be accounted for.

2.3.4 Cryogenic separation

Cryogenic separation units are operated at extremely low temperature and often at high pressure to separate components according to their different boiling temperatures. In our case, producer gas would be cooled down and sent to de-methanizer. The top fraction of de-methanizer is then feed to the system based on Black&Veatch, Coal to LNG process. (See Appendix A.1.2). Therefore, in this case LNG would be acquired as a product. The advantage of this approach is that the remaining syngas (essentially H2 and CO). Therefore, it would be reasonable to use it for a different kind of synthesis. (i.e. methanol production).

However, prior to cryogenic distillation section, gas is needed to be cleaned from carbon dioxide and water to very low levels to avoid plugging by solidified CO2 and water. The usual minimum specifications are 50ppm for carbon dioxide and 1 ppm for water. This involves additional capital cost in the gas cleaning section. Water content is reduced to low level via molecular sieve, while carbon dioxide typically either with PSA, or specially designed amine scrubbing system or combination of the two.
Nevertheless, the highest cost lies in the utility section for cooling down the gas to the temperature needed for cryogenic distillation. On smaller scale, typically mixed refrigerants are used as cooling medium. Temperature approach is usually around 2°C in order to minimize work needed in compression section of refrigerant cycle. In order to reduce the operating cost, process is highly integrated which diminish flexibility for different feed compositions. Additionally, separation of C2+ fraction is presumed not to be economical on the small scale, due to low relative volatility between ethane, ethylene and acetylene.
2.4 Comparison of the options

In the following table advantages and drawbacks of the short list of options have been summarized:

Table 1: Overview of the possible options

<table>
<thead>
<tr>
<th>Advantages:</th>
<th>OPTION 1 Ethyl-benzene production</th>
<th>OPTION 2 Aromatization</th>
<th>OPTION 3 Hydroformylation</th>
<th>OPTION 4 Cryogenic separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>More valuable products</td>
<td>More valuable products</td>
<td>More valuable products</td>
<td>Possibility of LNG as a product instead of SNG</td>
<td></td>
</tr>
<tr>
<td>Products easily separated from the producer gas</td>
<td>Products easily separated from the producer gas</td>
<td>Product easily separated from the producer gas</td>
<td>High purity of syngas</td>
<td></td>
</tr>
<tr>
<td>Easily integrated into the Biomass-SNG system</td>
<td>Zeolite catalyst: cheap and robust</td>
<td>Zeolite catalyst: cheap and robust</td>
<td>Mature technology</td>
<td></td>
</tr>
<tr>
<td>Zeolite catalyst: cheap and robust</td>
<td>Heterogeneous catalysis: cheap and simple reactor</td>
<td>Heterogeneous catalysis: cheap and simple reactor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heterogeneous catalysis: cheap and simple reactor</td>
<td>Possible high conversion of ethylene</td>
<td>Possible high conversion of ethylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Easily integrated into the Biomass-SNG system</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Drawbacks:</th>
<th>OPTION 1 Ethyl-benzene production</th>
<th>OPTION 2 Aromatization</th>
<th>OPTION 3 Hydroformylation</th>
<th>OPTION 4 Cryogenic separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additional benzene required</td>
<td>Mixed products</td>
<td>Homogeneous catalysis</td>
<td>Separation of C2+ fraction not economically feasible on small scale</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mixed products</td>
<td>Difficult separation of the catalyst</td>
<td>Very low specification of CO2 and water</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expensive catalyst</td>
<td>Limited flexibility due to high level of integration</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>High operating costs</td>
<td></td>
</tr>
</tbody>
</table>
2.5 Preliminary economic evaluation

Rough mass balances for 100MW plant input have been done. The results are presented in Table 3. A complete conversion of ethylene to products\(^4\) was assumed. In Table 2, the assumed prices of possible products are given.

Table 2: The assumed prices of possible products

<table>
<thead>
<tr>
<th></th>
<th>CH4</th>
<th>C2H4</th>
<th>Benzene</th>
<th>EB</th>
<th>LNG</th>
<th>Methanol</th>
<th>Propanal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price [$/t]</td>
<td>400</td>
<td>1250</td>
<td>1300</td>
<td>1400</td>
<td>500</td>
<td>400</td>
<td>900</td>
</tr>
</tbody>
</table>

Table 3: Preliminary estimation

<table>
<thead>
<tr>
<th></th>
<th>FEED [kmol/hr]</th>
<th>SNG case</th>
<th>BTX case</th>
<th>EB case</th>
<th>DEA case</th>
<th>HF case</th>
<th>CRYO case</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>106</td>
<td>307</td>
<td>274</td>
<td>217</td>
<td>217</td>
<td>194</td>
<td>0</td>
</tr>
<tr>
<td>CO</td>
<td>246</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H2</td>
<td>193</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C2H4</td>
<td>35</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>35</td>
</tr>
<tr>
<td>BTX</td>
<td>8</td>
<td>0</td>
<td>8</td>
<td>-27</td>
<td>18</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>EB</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>35</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LNG</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>106</td>
</tr>
<tr>
<td>Propanal</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>35</td>
<td>0</td>
</tr>
<tr>
<td>Methanol</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>146</td>
</tr>
<tr>
<td>M$/y</td>
<td>-14(^6)</td>
<td>16</td>
<td>20</td>
<td>31</td>
<td>25</td>
<td>31</td>
<td>38</td>
</tr>
<tr>
<td>Difference to ref. case</td>
<td>0</td>
<td>4</td>
<td>15</td>
<td>9</td>
<td>15</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>

Results in Table 3, are given for a 100MW plant assuming 8000 hours in operation. They are used only an indication. They show price difference of the possible products for different options in ideal case. The capital and operating costs are not considered. Chapter 5 will describe the complete economic picture.

\(^4\) Ethylbenzene, Aromatization and Hydroformylation case

\(^5\) 400 $/t equals to 7.55$/GJ LHV basis

\(^6\) Negative number represents the cost of biomass; 5 $/GJ
2.6 Selection

As it could be seen from the preliminary analysis, which was previously presented in Table 3, all of the suggested options have an economic driver for the further evaluation.

It has also been noticed that economic driver increases with the complexity of the process. If number of equipment needed is considered as sign of the complexity of the process, then sequence BTX, DEA, EB, HF, CRYO follows the sequence of price difference of the possible products. However, the capital costs are also expected to follow the same pattern.

However, it is important to mention that each of the alternative options will reduce part of the capital costs of the reference case, due to the fact that two catalytic reactors in the reference case can be omitted (HDS and reformer).

Hydroformylation case (Option 3) has a similar economic driver as EB production case (Option 1) but since it employs a homogenous catalysis, it is more complex process. Basically, in HF case we are solving a problem for difficult ethylene separation but at the same time we are creating issue of difficult separation of the catalyst. The novel processes that could overcome this obstacle were not included since they are still in the phase of development.

Due to the high complexity and number of units needed, cryogenic separation (Option 4) is expected to have highest capital costs and a lower chance of success, despite the obvious benefits in differences in prices of possible products. Nevertheless, it is important to design the process and make a proper estimation of the investments.

Ethylbenzene production (Option 1) and aromatization of ethylene (Option 2) were selected as the most promising ones from the combination of added value and expected limited increase in capital and operating costs. The fact that those options “only” involve zeolite catalysts is an important argument for selection of these processes. It offers a possibility for a co-production to be placed upstream since it can deal with not yet ultra clean gas. Between those options, ethylbenzene production is a more complex one but potential economic benefits are higher.

Therefore, both of these options were considered for the further study. Those options were considered to have biggest chance for success from technological and economical perspective. Furthermore, they can be easily integrated into the current SNG process scheme while offering economic benefits.

BTX, DEA, EB, HF, CRYO stands for BTX removal, Diluted Ethylene Aromatization, Ethylbenzene production, Hydroformylation and Cryogenic separation respectively.
3

Experimental work

3.1 Planning of the experiments

As mentioned before, both of the selected options use zeolites as catalysts. Nearly half of the patents in the field of synthesis of specialty chemicals on zeolites concern ZSM-5, known for its low coking activity [12]. ZSM-5 based catalysts are often used in vapour phase alkylation and offer low coking tendency and therefore life cycles between regeneration are possible [13]. Hence, ZSM-5 was selected as a reasonable choice for performing the first experiments.

However, in all research papers that were addressing aromatization of diluted ethylene, benzene was not present in the gas stream. On the other hand, alkylation of benzene with diluted ethylene was always performed with the excess of benzene. As stated before, ethylene concentration in producer gas exiting OLGA is usually four to eight times higher than benzene concentration. It can be considered that conditions in our system are between these two selected options; aromatization and alkylation. Hence, first experiment was needed to demonstrate the behaviour of the system with these inlet feed conditions.

Therefore, the following experiments were planned:

- Test 1: Experiments with the current ratio of ethylene and benzene in the producer gas

- Test 2: Experiments with the addition of benzene (stoichiometric ratio of ethylene and benzene 1:1)

These experiments were planned to be performed by using ZSM-5 with lower Si/Al ratio. That means, that catalyst is more active, but at the same time also more susceptible to deactivation by coking. [13]

Later on, it was planned to perform the same experiments, using ZSM-5 with higher Si/Al ratio (Test 3).
3.2 Experimental setup

Zeolite ZSM-5 was provided by “Zeolyst International”\(^8\). Following two samples were tested:
- CBV 3014E CY (Si/Al ratio 15, 1.6 mm extrusions with 20 % binder)
- CBV 8014 CY (Si/Al ratio 40, 1.6 mm extrusions with 20 % binder)

Experiments were performed in a stainless steel tubular reactor of 26mm internal diameter, heated by electrical furnaces. 20 g of catalyst was loaded into the reactor. The reactant and product gas composition was analysed with microGC equipped with TCD detectors. The concentrations of lower hydrocarbons\(^9\) and sulphur compounds were measured offline with GC set equipped with FID detectors. The concentrations of higher aromatics\(^10\) were measured offline with SPA\(^11\) sampling method. The conditions in reactor were as follows: temperature= 360-450°C, pressure=1 bar, WHSV=3 h\(^{-1}\).

In the Figure 6 scheme of the experimental setup is given.

![Scheme of the experimental setup](image)

Figure 6: Scheme of the experimental setup

Producer gas exiting OLGA tar removal section is cooled down to 5°C which reduces water content to around 5000ppm. Since zeolites are basically solid acids, it is needed to purify the stream from ammonia which is considered to be a weak base. Therefore, before entering the reactor the producer gas is cleaned from ammonia with HNO\(_3\) solution. Neon flow of 5 ml/min was supplied to the

\(^8\) [www.zeolyst.com](http://www.zeolyst.com)

\(^9\) Propane, propylene, propadien, butane, iso-butane, C4 olefins, pentane, C5 olefins

\(^10\) The concentration of benzene and toluene were measured by micro GC

\(^11\) Solid Phase Adsorption method
system as an internal standard. Upper part of the reactor was filled with inert alumina\(^{12}\) which acted as a heating zone. Temperature in the catalyst bed was measured with set of 4 thermocouples, approximately 1cm apart in the axial direction.

### 3.3 Test 1: Influence of temperature

After reaching the stable condition in the MILENA gasifier, producer gas has been introduced to the tubular reactor. The MILENA gasifier was operating at \(T= 850\, ^\circ\text{C}\). Beechwood was used as a biomass feedstock.

The operating conditions in the tubular reactor were as follows:

Temperature=360°C, pressure=1 bar, WHSV=3h\(^{-1}\). Temperature was afterwards increased to 420°C. The catalyst used was ZSM-5 with Si/Al ratio of 15. The composition of the gas entering the reactor is given in the following table. The values have been corrected for the air leakage that was occurring in the gas analysis set.

| & H\(_2\) \(\%\) & CO \(\%\) & CO\(_2\) \(\%\) & CH\(_4\) \(\%\) & N\(_2\) \(\%\) & C\(_2\)H\(_4\) \(\%\) & C\(_2\)H\(_6\) \(\%\) & C\(_3\)H\(_6\) ppm & C\(_6\)H\(_6\) ppm & C\(_7\)H\(_8\) ppm & H\(_2\)S ppm & CO\(_S\) ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| & 21.1 | 35.4 | 21.5 | 11.79 | 3.1 | 4.0 | 0.23 | 0.38 | 0.07 | 5270 | 376 | 134 | 17 |

Duration of test was 4 hours. Figure 7 shows the conversion of ethylene during that period. In the same Figure inlet and outlet concentration of benzene and toluene are also given. The blue section on the graph represents the temperature of 360°C while the yellow section represents the temperature of 420°C. The product distribution of ethylene products and distribution between aromatics is given in Figure 8.

Figure 7: Conversion of ethylene; inlet and outlet concentrations of benzene and toluene; WHSV=3h\(^{-1}\); Ethylene/Benzene=7.8; ZSM-5 Si/Al=15

\(^{12}\) 99wt\% α\(\text{Al}_2\)O\(_3\), 0.2wt\% SiO\(_2\), 3mm diameter
The total C/H/O mass balance at 360°C gave a 97.5%, 97.4% and 97.1% match respectively.

As it can be seen in Figure 7 initial conversion was 95%. It was decreasing over time up to 81% where it remained stable. The initial drop or activity is assumed to occur because of the co-adsorption of other molecules present in the gas (mainly CO and CO₂). The desorption in nitrogen flow at 470°C was performed after the test.

It is possible that the drop in conversion is also influenced by temperature change. However, later tests (Test 3) showed the same pattern of the conversion drop at constant temperature.

At 360°C there was no significant change in benzene concentration. On the other hand, the complete conversion of acetylene has been noticed. It has been assumed that acetylene is being converted partially to ethylene and partially to small amount of tars that have been detected (naphthalene, cresol, methyl-naphthalene, etc.). This assumption is based on the work of Tsai and Anderson [14] which showed that the main products of acetylene reaction over ZSM-5 zeolites, in the presence of hydrogen, are ethylene, naphthalene and methyl-naphthalene.

From Figure 8 it can be noticed that the product of aromatics is different than in research work of Choudary [7] and Qiu [8] which address aromatization of diluted ethylene over ZSM-5 catalyst. In our experiment no production of benzene has been observed at 360°C. There is also a significantly higher concentration of ethyl-benzene and di-ethyl-benzene. Since in the inlet gas it was already 0.5% of benzene this difference in product distribution was expected. It can be concluded that benzene entering the reactor changes the equilibrium between aromatic interconversion reactions. Additionally much higher concentration of ethylbenzene and diethylbenzene are implying that parallel reactions of benzene alkylation are occurring. As shown in the Figure 7 there was no significant difference between benzene inlet and outlet concentration. Therefore, it can be concluded that, at 360°C, reaction rate of benzene production from ethylene aromatization and reaction rate of benzene alkylation to ethylbenzene are equal.
Product distribution of ethylene converted and distribution between aromatics were also measured at 420°C. The results are presented in Figure 9. The total C/H/O mass balance gave a 98.0%, 97.0% and 96.8% match respectively. It is needed to mention that at this moment conversion was lower (81%). Therefore, question remains if conversion has an influence on product distribution. However, based on the work of Choudary [9] it can be assumed that temperature has a dominant influence. The yield of aromatics only slightly increased at 420°C. However, looking at Figure 7 it can be observed that at higher temperature, benzene is also being produced. This is in accordance with the findings of Choudary [9] and Qiu [8], who showed that at higher temperature the product distribution is shifted towards lower aromatics.

Figure 9: Distribution of ethylene products;
WHSV=3h⁻¹; T=420°C; ZSM 5 Si/Al=15 ; Conversion =81%; E/B=7.8;

3.4 Test 2: Influence of benzene addition

The second test was planned to be performed with stoichiometric ratio of ethylene and benzene in the producer gas entering the reactor. Increasing the benzene concentration was planned to be done by feeding toluene into the MILENA gasifier. The main reason for taking this approach was due to safety issues. After reaching stable condition in MILENA gasifier toluene was feed to the gasifier with the mass flow of 200g/h and subsequently 600 g/h. However, the maximum increase of benzene concentration that was achievable with this approach was 0.6 mol% (total 1.1 mol%). This is far from the concentration of benzene needed for the stoichiometric ratio between ethylene and benzene (4 mol%).
The yellow section in the figure above represents the beginning of toluene feeding into the gasifier of 200 g/h while the green section represents the increase of toluene feeding to 600 g/h.

Total mass C/H/O balance for MILENA gasifier did not give a satisfactory match. However, increase of CO2 concentration of the flue gas in the combustion sector was clearly perceived. It is shown in the Figure 11. It indicates that additional carbon (from toluene) is transported to the combustion section and therefore is lost from the producer gas.

Figure 11: Concentration of CO2 and O2 in the flue gas

However, although desirable concentration in the inlet was not achieved, it was noticed that even small increase of benzene from 0.5% to 1.1% would increase aromatic distribution towards ethyl-benzene and di-ethyl-benzene significantly.
The conversion of ethylene was 87%, of which product distribution towards aromatics was 37%. The product distribution between aromatics is shown in the Figure 12.

![Figure 12: Distribution of aromatics products in case of benzene addition; WHSV=3h⁻¹; T=360°C; ZSM-5 Si/Al=15; Benzene inlet = 1.1 mol%](image)

Nevertheless, it is important to mention that toluene inlet concentration was increased as well, which would diminish toluene production in aromatization reactions due to equilibrium existing between the aromatic products. Therefore, it remains unknown what would be product distribution towards toluene in case when only benzene concentration is increased.

### 3.5 Test 3: Influence of catalyst acidity

Additional test was performed to test the stability of conversion during the longer period of time. Catalyst used in this case was ZSM with Si/Al ratio of 40. The composition of inlet feed to the reactor is given in Table 5.

<table>
<thead>
<tr>
<th></th>
<th>H₂ %</th>
<th>CO %</th>
<th>CO₂ %</th>
<th>CH₄ %</th>
<th>N₂ %</th>
<th>C₂H₂ %</th>
<th>C₂H₆ %</th>
<th>C₂H₄ %</th>
<th>C₃H₆ ppm</th>
<th>C₆H₆ ppm</th>
<th>C₇H₈ ppm</th>
<th>H₂S ppm</th>
<th>COS ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>28</td>
<td>27.7</td>
<td>27.8</td>
<td>10.2</td>
<td>2.6</td>
<td>2.8</td>
<td>0.13</td>
<td>0.19</td>
<td>0.03</td>
<td>5526</td>
<td>239</td>
<td>118</td>
<td>10</td>
</tr>
</tbody>
</table>

The conversion of ethylene and benzene during 6h test are given in Figure 13.
It has been noticed that initial conversion was lower than in previous cases (45% compared to 95%) as well as stable conversion (20% compared to 81%). That was expected, since zeolites with higher Si/Al ratio have lower acid site density, which implies lower activity. However, it must be stressed, that inlet conditions were not the same as in the previous cases. It can be noticed from Table 5, that ethylene inlet concentration was 31% lower than in the previous tests. Since reaction rate is dependent of the partial pressure of ethylene, lower inlet concentrations imply lower conversion. The sudden drop of ethylene was due to disturbance in the flow in the gas analysis system.

Additionally, during this test benzene conversion of approximately 50% was observed. The possible reasons are:
  - Higher Si/Al ratio favours the alkylation reactions
  - Lower E/B ratio favours the ethylbenzene production
  - Production of ethylbenzene is favoured at lower conversion of ethylene

However, additional experiments are needed to be performed in order to distinguish what is the dominant factor for this observed behaviour. Unfortunately, until now SPA samples are not being analysed, so distribution of aromatic products is not given in this version of the report.
3.6 Conclusions from the experimental results

The following conclusions have been made from the experimental work:

- The idea of reactive separation was proven
- High conversion of ethylene is achievable
- Selectivity towards aromatics was around 40%
- Acetylene is fully converted
- High temperature favours the production of lower aromatics
- Higher concentration of benzene at inlet are shifting the product distribution towards ethylbenzene
- Feeding toluene into the gasifier can increase benzene concentration in producer gas only up to the certain point

However, main insight of the experimental work performed was that reactive separation of diluted ethylene was proven as a concept. Ethylene as a small molecule with low boiling point is converted to large aromatic molecules with high boiling point.

The important aspect of the performed experiments is also that it gave insight for designing the process schemes, and background to support currently theoretical co-production schemes. In order to make co-production schemes more feasible it would be desirable to have high selectivity towards aromatics. Also high selectivity toward one aromatic product would be desirable, because of the higher price that we can get for pure products. The certain conclusions have been made that showed the way to achieve it.

Even though we did not manage to achieve the conditions when benzene is in excess compared to ethylene, there is a clear indication that additional benzene would increase selectivity towards ethylbenzene significantly.

Therefore, two possible routes are possible:

- Developing the catalyst in order to achieve high selectivity towards aromatics and optimizing reactor conditions in order to increase selectivity towards one product.
- Supplying the additional benzene to the system in order to increase selectivity towards one product (ethylbenzene)
4 Process design

In the following subchapters process scheme of the current Biomass-bioSNG system is given with a short description. Gradually, the alternative co-production schemes are being introduced and described briefly. The newly developed process schemes ethylbenzene production (EB case) and diluted ethylene aromatization (DEA case) are presented in Chapter 4.2.2. and Chapter 4.2.3. Their development was based on literature study, insights gained from the lab experiments and principles of process synthesis. The unit used in all of the process schemes are described in more details in Appendix A.2.

4.1 Reference case

Figure 14: Reference case process scheme

The reference process considers that SNG is the only product made from biomass gasification. The block flow diagram of the process is shown in Figure 14. Here we can see that after gasification and tar removal, the gas is cooled to 25 °C. and further compressed to a pressure of 7 bar. After compression some water will condense out from the gas stream, while the gas at high temperature, obtained in the last compression stage, is sent to an adsorption unit where HCl is retained on ZnO+Na₂O/Al₂O₃ adsorbent at 180 °C such that in the outlet the composition of HCl is 1 ppm (mol) or lower. After the HCl removal, the gas is sent to hydrodesulphurisation (HDS) unit where organic-S is converted to H₂S. At the same time, it is considered that HDS catalyst has shift and hydrogenation activity of unsaturated hydrocarbons (benzene is not hydrogenated). In the following step, H₂S is retained by chemical adsorption on
ZnO and the product gas free of \( \text{H}_2\text{S} \) is sent to a reforming unit, where heavy hydrocarbons (e.g., benzene, toluene) are reformed into smaller molecules (\( \text{CH}_4, \text{CO}, \text{CO}_2, \text{H}_2 \)). In addition, water gas shift (WGS) also occurs in the reforming. The product of the pre-reformer is sent to the first methanation step, since it is free of \( \text{H}_2\text{S} \) and other components that may deactivate the methanation catalyst (\( \text{HCl}, \text{benzene} \)). At the same time, the feed to 1\textsuperscript{st} methanation step is at high temperature and contains a significant amount of water to prevent soot formation, and this is an advantage compared to the case when 1\textsuperscript{st} methanation would be carried out after \( \text{CO}_2 \) separation. After the first methanation step, \( \text{CO}_2 \) is removed by amine scrubbing. The amount of \( \text{CO}_2 \) removed is such that stoichiometric ratio between the components \( (\text{CO}, \text{CO}_2, \text{H}_2) \) participating in the methanation is at stoichiometric value. After the last methanation step, the SNG product is compressed to 60 bar.

### 4.2 Co-production schemes

#### 4.2.1 BTX removal case

![Figure 15: BTX removal process scheme](image)

Compared to the reference case, in this process layout the benzene and other heavy organic components are removed from the stream leaving the tar removal unit (see Figure 14). Benzene separation is carried out by washing it out with a solvent. The product stream, free of benzene is cooled to \( 25^\circ \text{C} \) to condense out the water, and further sent through an active carbon bed to retain all the heavy components that could not be washed out with benzene. After compression to 7 bar, the \( \text{HCl} \) is removed by adsorption similar as in the reference case. The product stream free of \( \text{HCl} \) is sent to a WGS reactor, and for this purposes some steam is added. Besides WGS, in the same reactor hydrogenation of unsaturated hydrocarbons (ethylene) occurs. One difference with the reference case is that WGS and hydrogenation takes place in the presence of \( \text{H}_2\text{S} \), which is possible on Co/Mo-S catalyst. Due to this, the first methanation step is no longer in front of \( \text{CO}_2 \) separation. However, the advantage of this process is that \( \text{H}_2\text{S} \) can be removed together with \( \text{CO}_2 \) in the amine-scrubbing unit minimizing the use of ZnO for \( \text{H}_2\text{S} \) separation. After \( \text{CO}_2 \) removal and compression to 40 bar still a guard bed is needed to protect the methanation catalyst. After the methanation, the SNG product is compressed to the imposed pressure of 60 bar.
4.2.2 EB case

Figure 16: EB case process scheme

Compared to the BTX removal case (see Figure 15), the difference is that producer gas leaving tar removal section is sent first to the ammonia removal unit. NH3 needs to be removed prior to zeolite catalyst. Because of the HCl and CO₂ present in the producer gas simple water scrubbing can be applied for that purpose. HCl is being removed as well so there is no need later on for a HCL adsorbent.

Gas is then compressed to 7 bar. Before the reactor, producer gas is mixed with benzene, in order to reach benzene to ethylene ratio of five. In the alkylation reactor, ethylene reacts with benzene over zeolite catalyst and produces ethylbenzene. Afterwards, excess of benzene and alkylation products are separated from the gas stream in the separation section (see appendix A.2.5). Separation section in the EB case consists of flash drum, distillation column and BTX scrubber. Ethylbenzene is taken as a product while benzene is recycled back to the alkylation reactor. Benzene from outside source is also added to the recycle stream. The gas stream is heading next to the Sour-WGS reactor. The difference in this case is that only small fraction of unconverted ethylene is being hydrogenated. That means more hydrogen in producer gas, which further implies less steam needed in the WGS reaction and less CO₂ removed in amine scrubber. In this case H₂S is also removed in the amine scrubbing unit. The producer gas is then sent to the methanation section. After the methanation, the SNG product is compressed to the imposed pressure of 60 bar.

4.2.3 DEA case

Figure 17: DEA case process scheme
This case can be considered as simplified version of EB case, previously described. Difference is that no benzene is supplied to the system and therefore there is no need for complicated separation system for benzene recycle.

After the DEA reactor, aromatics are removed via scrubbing oil. The gas stream is heading next to Sour-WGS reactor. Steam is added and WGS reaction is occurring. In the same reactor unconverted ethylene and lower unsaturated hydrocarbons produced are being hydrogenated. Subsequently, producer gas is feed to the amine scrubber where H2S and excess of CO2 are removed. At this point producer gas is cleaned from olefins, aromatics, higher compounds and H2S and it has a right M ratio for the methanation reaction. The gas is compressed to 40 bar and sent to the methanation section. After the methanation, the SNG product is compressed to the imposed pressure of 60 bar.

The short overview of the differences between all the options described is given in Appendix 0.

4.3 AspenPlus modelling

AspenPlus 8.2 has been used for the flowsheet calculations, with SRK chosen as the thermodynamic model and the steam tables obtained from STEAMNBS. The volume percentages of feed (OLGA gas) were the same as in the reference case. The PFDs and heat & mass balances can be found in Appendix 0.

The following three cases were assessed:

- **EB: Ethylbenzene production case** (see Figure 16)
  - EB-1: Conversion of ethylene and selectivity to ethylbenzene obtained from the literature [15]

- **DEA: Aromatization of diluted ethylene** (see Figure 17)
  - DEA-1: Conversion of ethylene and distribution of the products obtained from the lab experiments
  - DEA-2: Conversion of ethylene selectivity to aromatics products obtained from the literature [8]
    Distribution between aromatics obtained from the lab experiments

General descriptions of the units used in all process schemes and assumption that have been made in AspenPlus model are given in Appendix A.2.
4.4 Results of AspenPlus simulation

The results of the AspenPlus simulations are given in Table 6. In the same table, in the first two columns, the simulation results from A. Motelica [16] for the Reference and BTX removal case are also given. These results will be used as an input for the cost estimate and comparison in the following chapter.

Table 6: The results of the AspenPlus simulations

<table>
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<tr>
<th></th>
<th>SNG - Base case</th>
<th>BTX case</th>
<th>EB - 1 case</th>
<th>DEA-1 case</th>
<th>DEA-2 case</th>
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<td></td>
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<td>DEB 4.9</td>
<td>X 4.9</td>
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<tr>
<td>Benzene added [kg/hr]</td>
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<td></td>
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<tr>
<td>Steam available [kg/hr]</td>
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<td>5102</td>
<td>2815</td>
<td>7708</td>
<td>8507</td>
</tr>
<tr>
<td>Electricity [MW]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(compressors and pumps)</td>
<td>3.63</td>
<td>3.55</td>
<td>3.52</td>
<td>3.50</td>
<td>3.49</td>
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<td>CO2 removed [kg/hr]</td>
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<td>12267</td>
<td>11309</td>
<td>11689</td>
<td>11268</td>
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</table>

B: Benzene  
T: Toluene  
X: Xylene  
EB: Ethylbenzene  
DEB: Diethylbenzene
The cost comparison of reference case with alternative process schemes has been done. The effects of co-production schemes on Total Capital Investment and Variable cost have been evaluated in the following subchapters.

5.1 Total Capital Investment

The Total Capital Investment constitutes multiple factors, as shown in Table 7. Typical breakdown of costs for a similar type of plant is also given. [17]

Table 7: Average breakdown of Total Capital Investment, as used for this study

<table>
<thead>
<tr>
<th>TOTAL CAPITAL INVESTMENT</th>
<th>Fixed Capital Investment</th>
<th>Indirect Costs</th>
<th>Working Capital</th>
<th>Start-up Costs</th>
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<td>Direct Costs</td>
<td>Indirect Costs</td>
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<tr>
<td>ISBL costs (on-site)</td>
<td>OSBL Costs (off-site)</td>
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<td></td>
</tr>
<tr>
<td>Purchase &amp; Installation</td>
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</tr>
<tr>
<td>of</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Process equipment</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>• Piping &amp; appurtenances</td>
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<tr>
<td>• Instrumentation &amp;</td>
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<td></td>
</tr>
<tr>
<td>Controls</td>
<td></td>
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<tr>
<td>• Electric equipment &amp;</td>
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<tr>
<td>materials</td>
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<tr>
<td>• Civil &amp; structural</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>• Process Buildings</td>
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</tr>
<tr>
<td>Yard Improvements</td>
<td>Up-front R&amp;D</td>
<td>Inventories</td>
<td>Modifications</td>
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<td>Auxiliary buildings</td>
<td>Up-front license</td>
<td>Salaries/wages due</td>
<td>Start-up labour</td>
<td></td>
</tr>
<tr>
<td>Service facilities</td>
<td>Equipment design and</td>
<td>Receivables less payables</td>
<td>Loss in production</td>
<td></td>
</tr>
<tr>
<td>Storage &amp; distribution</td>
<td>engineering</td>
<td>Cash</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Land</td>
<td>Construction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Contractor’s fee</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Contingencies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45% of TCI</td>
<td>20% of TCI</td>
<td>18% of TCI</td>
<td>10% of TCI</td>
<td></td>
</tr>
<tr>
<td>100%</td>
<td>44% of ISBL</td>
<td>40% of ISBL</td>
<td>22% of ISBL</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16% of ISBL</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
There are two approaches for estimating Total Capital Investment of a bioSNG plant:

- From reference data of technologically similar facilities, applying different factors to cope with different scale, start-up year, etc.
- Bottom up method, where basic engineering is carried out for the plant and cost estimation are based on process, flow diagram, energy and mass balances, and quotes for major equipment.

In the report from G. Aranda [18] the first method was pursued in order to get a first estimation of the costs for bioSNG plant. Total capital investment was estimated to be 1100$\_2013/kW\text{input}$. This value has been estimated for a 1GW scale of input. Scaled down to 100 MW (input biomass for AspenPlus simulations) it gives Total Capital Investment cost of 220 M$.

It can be assumed that co-production does not have an effect on working capital cost and start-up costs. Regarding the OSBL costs (off-site), small increase in costs can occur because of the storage capacity needed for the co-products. However, due to the small scale of the plant considered in this study it is expected to be insignificant.

Indirect costs include the construction of the plant, contractor’s fees, etc. These also include R&D, design and engineering of the equipment, and licenses. Comparing the co-production schemes, we can assume that only EB case could have higher indirect cost than reference case. This is due to the fact that EB case is more complex due to the separation sector. For other two alternatives, it is anticipated to have same indirect cost as the reference case.

If we consider breakdown of the TCI for a 100 MW, according to Table 7, we are getting ISBL costs of 99 M$. Deducting from that amount, the typical costs for piping, civil and structural, instrumentation and control, gives cost of 88 M$ for purchase and installation of all process equipment. MILENA and OLGA are considered to make 40% of those costs\textsuperscript{13}. Therefore, since modifications of our system are located downstream of OLGA, it can be concluded that alternative schemes are not changing the TCI significantly.

This is even more expressed when impact of added equipment on rest of the process is taken into consideration. For example, adding equipment like BTX scrubber will remove other unit like reformer and HDS. Or else, removing ethylene and benzene from the stream, would diminish SNG production, but at the same time methanation section would be smaller and, therefore, cheaper. Additionally, both of the zeolite reactors in the proposed schemes are fixed bed reactors; therefore it is not expected to contribute significantly to the total equipment costs.

Finally, it can be concluded that alternative co-production schemes proposed are not expecting to have a significant influence on TCI; except in EB case where minor additional TCI cost are anticipated due to the separation sector for benzene recycle.

\textsuperscript{13} Internal data
5.2 Variable costs

The comparison of variable costs was based on the results from the Aspen simulation and certain assumptions. The results from the evaluation are presented in Table 8. The prices of the catalysts and assumptions that had been made are given in Table 9.

Table 8: Variable costs for all cases in k$/y

<table>
<thead>
<tr>
<th>K$/y</th>
<th>SNG</th>
<th>BTX</th>
<th>EB</th>
<th>DEA-1</th>
<th>DEA-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost of ZSM5</td>
<td>0</td>
<td>0</td>
<td>403</td>
<td>341</td>
<td>0</td>
</tr>
<tr>
<td>Cost of GA/ZSM5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>504</td>
</tr>
<tr>
<td>Cost of reformer catalyst</td>
<td>1834</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cost of electricity compressors</td>
<td>2262</td>
<td>2222</td>
<td>2216</td>
<td>2191</td>
<td>2212</td>
</tr>
<tr>
<td>Cost of electricity amine scrubber</td>
<td>202</td>
<td>189</td>
<td>175</td>
<td>180</td>
<td>174</td>
</tr>
<tr>
<td>Cost of electricity BTX removal</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Cost of Cl adsorbent</td>
<td>19</td>
<td>19</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cost of H2S adsorbent</td>
<td>79</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cost of make-up BTX scrubber</td>
<td>0</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Cost of make-up amines</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Sum of operating cost</td>
<td>4416</td>
<td>2604</td>
<td>2968</td>
<td>2886</td>
<td>3064</td>
</tr>
</tbody>
</table>

From the Table 8 it can be realized that all of the alternative schemes have a noticeably lower operating costs. The main reason for the higher operating costs in the reference case is due to the reformer catalyst cost. Difference in operating cost between two DEA cases is because DEA-2 case uses zeolite catalyst with 5% impregnated gallium in order to achieve higher selectivity. The reason for assuming different weight hourly space velocities for EB and DEA cases was due to the fact that reaction rate of alkylation reaction increases with higher partial pressure of benzene.

Table 9: Prices and assumption used for variable cost estimate

<table>
<thead>
<tr>
<th>Price</th>
<th>Assumption used:</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM 5</td>
<td>60 $/kg</td>
</tr>
<tr>
<td>ZSM/Ga 5wt%</td>
<td>89 $/kg</td>
</tr>
<tr>
<td>Reformer catalyst</td>
<td>195 $/kg</td>
</tr>
<tr>
<td>Cl and S adsorbent</td>
<td>170 $/ton</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.075 $/kWh</td>
</tr>
<tr>
<td></td>
<td>EB 1: WHSV=3h⁻¹, two reactors; catalyst lifetime of 3 years</td>
</tr>
<tr>
<td></td>
<td>DEA 1 : WHSV=2h⁻¹, two reactors; Catalyst lifetime 3 years</td>
</tr>
<tr>
<td></td>
<td>DEA 2 : WHSV=2h⁻¹, two reactors; Ga price 280$/kg; Lifetime of 3 years</td>
</tr>
<tr>
<td></td>
<td>NSHV=500; Bulk density=750 kg/m³; Catalyst lifetime of 3 years</td>
</tr>
<tr>
<td></td>
<td>13% adsorbing capacity</td>
</tr>
</tbody>
</table>
5.3 Production cost estimation

In the following table the final result of cost evaluation are given.

<table>
<thead>
<tr>
<th></th>
<th>SNG</th>
<th>BTX</th>
<th>EB</th>
<th>DEA-1</th>
<th>DEA-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCI annually</td>
<td>22000</td>
<td>22000</td>
<td>22500</td>
<td>22000</td>
<td>22000</td>
</tr>
<tr>
<td>Operating costs</td>
<td>4416</td>
<td>2604</td>
<td>2968</td>
<td>2886</td>
<td>3064</td>
</tr>
<tr>
<td>Fixed</td>
<td>3300</td>
<td>3300</td>
<td>3375</td>
<td>3300</td>
<td>3300</td>
</tr>
<tr>
<td>Biomass</td>
<td>14400</td>
<td>14400</td>
<td>14400</td>
<td>14400</td>
<td>14400</td>
</tr>
<tr>
<td>Total cost</td>
<td>44116</td>
<td>42304</td>
<td>43243</td>
<td>42586</td>
<td>42764</td>
</tr>
<tr>
<td>BTX</td>
<td></td>
<td>-5974</td>
<td>17880</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AROM</td>
<td></td>
<td></td>
<td>-9029</td>
<td>-12651</td>
<td></td>
</tr>
<tr>
<td>EB</td>
<td></td>
<td></td>
<td>-36605</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNG produced [PJ/y]</td>
<td>2.00</td>
<td>1.78</td>
<td>1.43</td>
<td>1.63</td>
<td>1.53</td>
</tr>
<tr>
<td>Cost SNG [$/GJ]</td>
<td>22.1</td>
<td>20.4</td>
<td>17.1</td>
<td>20.6</td>
<td>19.7</td>
</tr>
</tbody>
</table>

Following assumption were made in the cost evaluation presented above:

- Interest and depreciation 10 % of the total capital investment\textsuperscript{14}
- Operating hours: 8000h
- Biomass cost: 5 $/GJ
- BTX price: 1100 $/tonne
- Ethylbenzene price: 1250$/tonne
- Mixed aromatics price: 1100$/tonne
- 5 M$ higher TCI for EB case\textsuperscript{15}

It can be seen that all of the co-production schemes offer a reduction in production costs of bioSNG.

It has been shown that EB case is a favourable one, offering a reduction in production cost of 5$/GJ, even when additional TCI costs are accounted. On the other hand, results of the economic analysis depend significantly on the assumed prices of the co-products.

Ethylbenzene prices are not easily found in open literature. However, as can be seen in Appendix A.5.1, price of styrene is mainly influenced by benzene price. The average price difference between styrene and benzene is around 250$ to 300$ per tonne. Limited data found in literature\textsuperscript{16} showed that that ethylbenzene to benzene price difference is around 100-200$ per tonne. Therefore, it can be considered that assumed prices used in this economic

\textsuperscript{14} Due to simplicity reasons; it is equal to an interest rate of 5.5% and depreciation period of 15 years

\textsuperscript{15} It is a combination of cost analysis of the distillation column in Aspen-Icarus and Indirect costs of 18% TCI

\textsuperscript{16} www.icis.com
assessment were reasonable. The influence of price difference between ethylbenzene and benzene on SNG production costs is also presented in Appendix A.5.1.

DEA-1, which used first results from lab experiments as an input, show to be less feasible than BTX removal. Still, evaluation of DEA-1 case was performed with first lab results, which were not optimized.

DEA-2 case proved to offer more cost benefit than BTX case. However, price considered for mixed aromatic products was the same as price assumed for co-products in BTX case (91% benzene, 9% toluene).

In Figure 18 influence of co-product price on SNG production costs is presented. In same figure, for EB case it is assumed that price difference between ethylbenzene and benzene is 150 $/tonne.

![Graph showing influence of co-product prices on SNG production costs; Biomass=5$/GJ](image)

As it can be seen from Figure 18, co-production schemes offer the savings in production costs of SNG, even when low prices are assumed for co-products.

Nevertheless, price of the biomass has also a lot of influence on feasibility of co-production schemes, particularly when acquired prices of co-products are low. (see Appendix A.5.2)
Ethylbenzene production and aromatization of ethylene were selected as the most promising options for separation of valuable co-products in the MILENA-OLGA to bioSNG system. They were selected as the best combination of added value and expected limited increase in capital and operating costs. Additionally, they were considered to be most easily integrated into the current biomass to bioSNG system. The fact that those options “only” involve zeolites, offers a possibility for a co-production to be placed upstream since it can deal with not yet ultra clean gas.

The experiments were planned and performed in order to prove the concept of reactive separation technique. Ethylene conversion of 95% was achieved. It has been shown, that 40% of ethylene is converted to aromatics. Additionally, influence of temperature, addition of benzene and catalyst acidity has been tested. It has been shown, that distribution between aromatics can be influenced with temperature and benzene addition.

Based on the insight obtained from experimental results, coupled with knowledge gained from literature study and following the principles of process synthesis, two new co-production schemes in Biomass to bioSNG were created:

- Ethylene benzene production process scheme (EB case)
- Diluted ethylene aromatization process scheme (DEA case)

The economic benefits of co-producing chemicals in a 100MW plant of biomass thermal input have been quantified. It was shown that their influence on TCI is limited while at the same time co-productions schemes are reducing operating costs mainly because catalytic reformer is omitted.

Ethylbenzene production case was selected as favourable option with the possibility to reduce production cost of bioSNG up to 5$/GJ.
It was shown that all of the co-production schemes offer a reduction in SNG production costs. However, reduction in production costs varies significantly with prices of co-products and price of biomass.

Nevertheless, they offer a substantiate reasoning to evaluate the proposed co-production schemes in more details. Furthermore, promising results from the first experiments offer a solid backbone that those options are plausible. Therefore, they offer a potential for future research. Further development is needed, optimization of catalyst and operating condition. Longer experiments need to be performed in order to assess catalyst lifetime between regeneration.

Finally, the results of this research were only one of the first steps in achieving the co-production of bio-chemicals in Biomass to SNG system. However, the one can imagine that after a persevering development of co-production of biochemical, it can make bioSNG more competitive to other energy sources.
Bibliography


Appendix A.

A.1. Co-production options

A.1.1 Hydroformylation case

Figure 19: Process scheme of Oxo process n-butyraldehyde production process
A.1.2 Cryogenic case

Figure 20: Process scheme of Black&Veatch Coal to LNG process
A.2. Description of units in the process schemes

A.2.1 MILENA gasifier (all cases)

MILENA is an allothermal gasifier developed by the Energy Centre of the Netherlands (ECN). Its development started in the late 1990’s based on the experiences of the SilvaGas and the FICFB (Güssing) technologies. Result was lab-scale MILENA in 2004 of approximately 25KWth input capacity and a pilot-scale place in 2008 of 800KWth capacity. Both of the gasifiers are connected with OLGA technology for tar removal.

It was designed as a first step in the production of synthetic natural gas (SNG). The gasifier contains separate sections for gasification and combustion. The gasification section consists of three parts (gasifier riser, settling chamber and downcomer) while combustion chamber consists only of one part. A scheme of the MILENA technology is shown in the following figure and it will be explained subsequently.

![Scheme of MILENA gasifier](image)

Biomass is fed into the gasifier riser. A small amount of superheated steam is added from below. Steam can be replaced by air if dilution of the producer gas is not a problem. Hot bed material (typically at 925°C) enters the riser through a hole, opposite of the biomass feeding point. The bed material heats the biomass to 850°C in the gasification section. The heated biomass particles degasify and are partially converted into gas. The bed material, together with the char is carried through the riser and separated from the producer gas in the settling chamber falling down into the downcomer and carried to the combustor. The typical residence time of the gas is several seconds.

17 Fast Internally Circulating Fluidised Bed
The combustor operates as a Bubbling Fluidized Bed. The downcomers transport bed material and char from the gasification section into the combustion. Tar and separated from the producer can also be fed into the combustor. Char, tar and dust are burned with air to heat the bed material to around 925°C. No additional heat input is required since all heat for the gasification process is produced by the combustion of the char, tar and dust. A typical MILENA gas composition, on dry basis, after tar removal, has been shown previously in Figure 2. Because steam was used as gasifier agent, the product gas contains only a small amount of N₂. As stated before MILENA gasifier was designed as a first step for the production of SNG. Therefore the high yield of CH₄ is very attractive.

MILENA gasifier had not been modelled in AspenPlus. Compositions and conditions of inlet and outlet streams from gasification sector were obtained from pilot plant results.

A.2.2 OLGA tar removal (all cases)

Tars can be considered as major technical obstacle in the implementation of biomass gasification technology. Condensing tars dramatically foul the downstream system piping and gas cooling and cleaning equipment, while liquid tar droplets (i.e. aerosols) that enter prime movers disturb the operation of these end-use applications of the product gas. Tar plays also negative role in the wastewater treatment problem. Removal of tar components wastewater requires considerable investments that can even be dramatic as some tar components show poisoning behaviour in biologic wastewater treatment systems (e.g. phenol).

Indirect combustion produces a combustible gas containing tar. Main reason for tars to survive is the low fluidized bed gasifier temperature (<1000 °C). Tar can be removed via conversion processes (thermal, catalytic or plasma) or via physical separation processes (absorption or condensation).

ECN started in 2001 with the development of the OLGA technology based on the later approach. This is an oil-based absorption system and it is meant to operate at temperature above water dew point, thus avoiding tar-water mixtures. OLGA is system consisted of series of three processes: condensation, aerosol removal and absorption.

OLGA tar removal section has not been modelled in AspenPlus. Compositions and conditions of inlet and outlet streams from removal section were obtained from pilot plant results.

A.2.3 Water scrubbing (EB, DEA-1, DEA-2 case)

In EB case and DEA-1 and DEA-2 ammonia needs to be removed prior to zeolite catalyst. Ammonia removal is usually performed with acid scrubber. However, because of the HCl and CO₂ present in the producer gas simple water scrubbing can be
applied for this purpose. Additional benefit is that hydrogen chloride will be removed as well.

NH₃ removal has been modelled in AspenPlus as separator block. 99.99% level of separation is assumed for both NH₃ and HCl.

### A.2.4 EB reactor (EB case)

The reactor system is comprised of two parallel fixed bed reactors. Zeolite ZSM-5 is used as catalyst, which has a low coking tendency and, therefore, life cycles between regenerations up to 120 days are expected. This was shown on the example on non-purified FCC off-gas, which was used as a diluted ethylene feedstock [5]. Catalyst activity can be renewed with when the deposed coke is burned off in air stream.

The kinetic data for alkylation of benzene on ZSM-5 found in literature [19] were tested with the input of relevant research papers [15]. Four sets of kinetic data were tested but results were unsatisfactory. It was concluded that kinetic data from literature are not suitable for extrapolation at different conditions.

Therefore, alkylation reactor has been modelled as R-STOIC reactor. Conversion of ethylene and selectivity towards ethylbenzene are assumed to be 95% and 90% respectively. This assumption was based on research paper from Graf [15]. The ratio of ethylene and benzene in the reactor feed was set to be 5. Pressure drop is assumed to be 1 bar.

### A.2.5 Separation section (EB case)

Separation section in the EB case consists of flash drum, distillation column and BTX scrubber (see appendix A.4.1). Before entering the distillation column the major part of the gases is removed by flash drum. Vapour stream from the flash drum, since it still contains a large part of the benzene, is sent to BTX scrubber for the recovery of benzene.

Liquid stream from the flash drum is fed to the distillation column. Since relative volatility between benzene and ethylbenzene decreases with higher pressures and temperatures, pressure in distillation column is set to 1 bar. Operating the distillation column at atmospheric pressure also decreases the temperature in the reboiler section, which implies that lower pressure steam can be used as utility. In the condenser section, cooling water of 20°C is used as coolant. Distillation column has 13 trays and feed at stage 9 is found as an optimum.

Top fraction of the distillation column (99% benzene) is mixed with the benzene recovered from the BTX scrubber and subsequently sent to evaporator. Vapour benzene is then sent back to the EB reactor.

### A.2.6 DEA reactor (DEA-1, DEA-2 case)
Diluted ethylene aromatization reactor is also considered to be system of two parallel fixed bed reactors. Catalyst used would be ZSM5 DEA-1, or ZSM impregnated with Gallium in DEA-2. It is unclear how much would be life cycles between the regeneration. Durability tests are needed to be performed for that purpose. It is assumed that catalyst activity can be fully restored after burning off the coke in the air stream.

No kinetic data was found in literature for aromatization of ethylene. Therefore, DEA reactor was modelled in AspenPlus as R-STOIC reactor with following assumptions:

DEA-1 case:

- Conversion of ethylene is assumed to be 81%, based on experimental results (see Chapter 3.3)
- Selectivity to aromatics is assumed to be 40% based on experimental results (see Chapter 3.3)
- Acetylene is assumed to convert partially to ethylene and partially to naphthalene

DEA-2 case:

- Conversion of ethylene is assumed to be 95%, based on literature [8]
- Selectivity to aromatics is assumed to be 80%
- Distribution between aromatics is assumed to be the same as in lab tests (see Chapter 3.3 Figure 9)
- Acetylene is assumed to convert partially to ethylene and partially to naphthalene

A.2.7 BTX removal/Aromatics removal (BTX, EB, DEA-1, DEA-2 case)

ECN recently started a development of technology for separation of bioBTX from the producer gas. The absorption was chosen as best technology for that purpose. Currently, there are lab scale absorber and stripper columns with 2m height. Dioxin was chosen as a first choice for absorber liquid.

However, dioxin that were used had problem with solidification on temperature around 50°C and issues with thermal stability [2]. Recent development of BTX scrubber managed to overcome these difficulties, by using silica based scrubbing oil. These improvements made system also suitable for separation of higher aromatics (DEA case), due to the higher temperature needed in the striping section. However, additional research and development of BTX scrubber still needs to be done.

BTX scrubber has been modelled in AspenPlus as separation block. It was assumed 99.9% removal with oil stripper, and rest removed with activated
carbon guard bed. Thiophene is also considered to be removed in the BTX unit [2].

A.2.8 HDS (reference case)/ Sour-WGS (BTX, EB, DEA-1, DEA-2 case)

HDS stands for Hydro DeSulphurization catalyst. It is used to convert organic sulphur components into smaller, inorganic sulphur components such as H$_2$S. Organic sulphur compounds in a typical producer gas from indirect gasification are CS$_2$, mercaptanes and thiophenes. One of the main organic sulphur components is thiophene (C$_4$H$_4$S). There are also variants of thiophene like methyl and ethyl thiophenes and the more complex benzo thiophenes. HDS catalysts are commonly used in the oil industry for sulphur conversion in liquid fuels which may contain several 1000’s of ppms of thiophenes. HDS reactors normally operate under high pressure (~20 – 80 bar) and moderate temperatures of around 350°C. HDS catalysts are also catalytically active in the hydrogenation of acetylene (C$_2$H$_2$) and ethylene (C$_2$H$_4$) into ethane and methane, and the water-gas shift (WGS) reaction. The hydrogenation and WGS activity cause a temperature increase across the reactor. Catalyst used is Cobalt Molybdenum$^{18}$ (CoMo) catalyst that —once partially sulfided— converts organic sulphur components at temperatures between 450°C and 600°C into H$_2$S. However, only in the reference case, (System 0A), it is needed to convert thiophene to H$_2$S. In other cases$^{19}$, thiophene is removed together with aromatics via scrubbing oil [2]. Therefore, since the only purpose for this reactor in those process schemes is hydrogenation of unsaturated hydrocarbon and Water Gas Shift reaction, it is regarded as Sour-WGS reactor.

Sour-WGS reactor was modelled in AspenPlus as R-GIBBS reactor. Pressure drop of 0.5 bar was assumed. The amount of steam added to the Sour-WGS is optimized in such way that M ratio in the producer gas after the CO2 removal is equal to 3.

$$M = \frac{[H2] - [CO2]}{[CO2] + [CO]}$$

A.2.9 Chloride removal (Reference, BTX case)

In Reference case and BTX removal case, hydrogen chloride has to be removed upstream of reformer and methanation reactor, since both catalysts demonstrated vulnerability for hydrogen chloride. It also needs to be placed before H$_2$S adsorption because hydrogen chloride could react with ZnO$^{20}$ to ZnCl$_2$, thus mobilizing the zinc content. Removal of Cl usually takes place down to a level below 1 ppm. Several commercial adsorbents are available, that

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$^{18}$ An alternative for CoMoS would be NiMoS

$^{19}$ BTX, EB, DEA-1, DEA-2 case

$^{20}$ A typical adsorbent for H$_2$S.
operate at different temperatures. Water scrubbing can be applied for the same purpose near "room" temperature (i.e. 20 - 50°C). In tests performed at ECN a commercial adsorbent consisting of ZnO+Na₂O/Al₂O₃ was used, for HCl removal at a temperature of approximately 180°C. Thermodynamic formation of ZnCl₂ is avoided because it typically takes place at temperatures above 225 °C.

A.2.10 Non-organic sulphur removal (Reference case)

In the reference case the main sulphur components that need to be removed after the HDS reactor are H₂S and COS. Depending on the type of biomass, producer gas from indirect gasification typically contains between 100 and 300 ppmv of H₂S. In the reference case, ZnO was selected as an adsorbent for sulphur removal (e.g. H₂S and COS). The type of ZnO used relate to hydrolysis activity to convert COS, CS₂, and organic sulphur into H₂S for efficient total-sulphur removal. It should reduce the total sulphur load in the producer gas to below 10 ppbV.

ZnO is a commonly applied commercial adsorbent upstream of natural gas reformers in fixed beds. The removal principle is based on the following equilibrium reaction: ZnO + H₂S ⇌ ZnS + H₂O We assumed that all sulphurous compounds are converted into H₂S (by the upstream HDS reactor). The ZnO section is typically operated below 400 °C, but still at relatively high temperatures to thermodynamically inhibit the activity for the water-gas shift reaction.

A.2.11 Amine scrubbing (All cases)

MEA (Monoethanolamine) is the preferred solvent for gas streams containing relatively low concentrations of H₂S and CO₂ and essentially without minor contaminants such as COS and CS₂. This is particularly the case when the gas is to be treated at low pressures and maximum removal of H₂S and CO₂ is required. MEA is widely used in the CO₂ removal from flue gasses where temperatures are moderate (~100 °C), pressures are near atmospheric and CO₂ concentrations typically are 5-15 vol%. The conditions for this application are very similar to the condition in the SNG design. CO₂ removal by MEA is a chemical absorption process and includes the following reactions:

\[
\begin{align*}
\text{MEA} + \text{H}_2\text{O}^- & \rightarrow \text{MEA}^- + \text{H}_2\text{O} \\
\text{CO}_2 + 2\text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}^- + \text{HCO}_3^- \\
\text{HCO}_3^- + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}^- + \text{CO}_2^- \\
\text{MEA} + \text{HCO}_3^- & \rightarrow \text{MEACOO}^- + \text{H}_2\text{O} \\
2\text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}^- + \text{OH}^-
\end{align*}
\]

Typical concentration of MEA ranges from 12 wt% to 32 wt%. MEA concentrations that exceed 32 wt% can become quite corrosive since the absorption of CO₂ makes the solution a strong acid. Hence, 30 wt% MEA is used to avoid severe corrosion. Another interesting aspect of MEA is the low absorption capacity for methane. For this reason these solvents are often used during sweetening of natural gas as well as the upgrading of biogas that has been produced through biomass digestion. For each ton of CO₂ captured
approximately 1.5 kg of fresh amine is required to make up for the loss by polymerization and binding to other acid components in the gas. The MEA waste stream should be significantly less for producer gas that has been cleaned already in previous steps.

The typical system that is used for CO\textsubscript{2} removal using MEA is an absorber / stripper combination. In such a system producer gas than needs to be purified is passed upward through an absorber column, counter current to a solvent solution (aqueous MEA solution). It is probably necessary to dry the gas prior to the absorber, in order to prevent dilution of the amine solution. Traces of NH\textsubscript{3} still present in the gas are most likely dissolved in the water, together with some HCN and HCl.

The rich MEA solution at the bottom of the absorber is heated by heat exchange with lean solution from the bottom of the stripping column and is then fed to the stripping column at some point near the top. Acid gas (CO\textsubscript{2}) that is removed from the MEA solution in the stripping column is cooled to condense the major portion of the water vapour. This condensate is fed back into the system to prevent the amine solution from becoming progressively more concentrated. Regeneration (stripping) of the MEA solution costs a fair amount of low grade heat. The typical heat required for stripping CO\textsubscript{2} from the MEA solution ranges from 3.0 to 4.0 MJ/kg CO\textsubscript{2}.

Amine scrubber was modelled in AspenPlus as separator block. Capture ratio of CO\textsubscript{2} was optimized together with amount of steam added to the Sour-WGS in order to reach M ratio of 3 needed for the methanation sector. The heat duty needed in the stripping section was assumed to be 3 MJ/kgCO\textsubscript{2} [20].

### A.2.12 Reformer (Reference case)

In the case when BTX are not removed prior to the methanation section, they need to be reformed since they are main soot precursor. These components are converted mainly into CO and H\textsubscript{2} by means of a reforming step. The reformer should operate at conditions at which no soot is produced, while steam is often added to prevent this. Selection of appropriate conditions at which no soot is formed is the most important aspect for smooth operation of the reformer. The water content of the gas before the reformer should be at least 40 to 50 vol%. A typical operating temperature to convert benzene and toluene, without the problems of soot formation lies around 500°C.

### A.2.13 Methanation (All cases)

In the methanation reactor(s), CO and CO\textsubscript{2} are converted to methane according to the following reactions.

\[
\begin{align*}
\text{CO} + 3\text{H}_2 & \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \\
\text{CO}_2 + 4\text{H}_2 & \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}
\end{align*}
\]
Depending on the process conditions, either the forward or reverse of the WGS reaction takes place:

\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \]

Low temperature and high pressure favour full conversion of CO and H\(_2\) to CH\(_4\). As the methanation reaction is highly exothermal, full conversion often requires execution in a number of steps with intermediate cooling. When the number of equilibrium stages increases, the CH\(_4\) content will increase. Recycling part of the product stream to the producer gas inlet can be used to limit the temperature increase, especially in the first step. Because of the high CH\(_4\) content already present in the stream which acts as a heat sink in the reactor, recycling stream can have lower flows.

The methanation technology, TREMP\textsuperscript{TM} by Haldor-Topsøe is used as a reference. The catalyst is Nickel based and should be able to withstand temperatures up to 700 °C in the first reactor. Further reactors operate at lower outlet temperatures to reach a high methane yield. When most of the CO is converted, excess H\(_2\) is consumed by reverse shift or direct methanation of CO\(_2\). The final SNG product must contain a small fraction of H\(_2\) to protect the catalyst against oxidation. At lower H\(_2\) concentrations, the heating value of the gas increases. Depending on the required SNG specifications the excess H\(_2\) can be kept in the product or has to be removed. When methanation is carried out at lower pressures, the adiabatic temperature increase will be lower. As a consequence the methanation could be operated adiabatically without gas recycles and in simple vessels without internal cooling. (System 0A)

An undesired side effect of the methanation reaction is soot or fixed carbon formation. The conditions that are mentioned above are such that fixed carbon (soot) could be formed through the following reactions:

\[ 2 \text{CO} \leftrightarrow \text{CO}_2 + \text{C}^{21} \]
\[ \text{CO} + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{C} \]

The top reaction, also called Boudouard reaction, is catalyzed by Fe, Ni and Cr and is supported by higher pressures. A way to suppress this reaction is to add steam or hydrogen to the gas. As mentioned before, cracking of olefins and aromatic components can also lead to carbon formation.

The sulphur specifications for the methanation catalysts are unsure. Relevant actors from Haldor Topsøe mention concentrations between 10 and 100 ppb [21]. However this depends on the type of sulphur components present as well as the accepted lifetime of the catalyst. For the purpose of this study, a specification of a total sulphur concentration in the gas of <10 ppbV is assumed, being a typical value mentioned in literature for catalyst specifications, and conform the final requirements for sulphur in the SNG.

\[21\] Boudouard reaction
Methanation sector was modelled in AspenPlus as a sequence of three R-GiBBS reactors with intermediate cooling. Pressure drop of 0.5 bar was assumed in every reactor. Recycle after first reactor is used to control the outlet temperature.
A.3. Differences between the process schemes

**Aromatics:**
In the reference case aromatics are reformed since they are coking precursors in the methanation sector. In all alternative schemes reformer is no longer needed since aromatics are removed prior to the methanation sector. BTX removal case and DEA case consider only BTX scrubber and subsequently active carbon guard bed for that purpose. In EB case, separation sector is comprised of flash vessel, distillation column, BTX scrubber and active carbon guard bed.

**Unsaturated hydrocarbons:**
Ethylene and other unsaturated hydrocarbons are hydrogenated in HDS unit in reference case, or in Sour-WGS reactor in BTX case. In the alternative schemes EB case and DEA case only small part of unconverted ethylene is hydrogenated. Additionally, in DEA case, other small unsaturated hydrocarbon are being formed which are also hydrogenated in Sour-WGS reactor.

**Ammonia and HCl removal:**
In EB case and DEA case ammonia needs to be removed prior to zeolite reactors. This is done by water scrubbing. However since HCl is also removed in this case, there is no need for HCl removal unit later on in the process (compared to reference case and BTX removal case). In reference case and BTX case, NH3 is not considered to be a problem and, therefore, is removed at last stages of the process. However, still it will create a waste water treatment issue.

**H2S removal:**
Since amine scrubber is positioned after the reformer, H2S in reference case needs to be removed with ZnO adsorbent prior to reformer. In alternative schemes (BTX,EB,DEA) the bulk of H2S is removed with amine scrubber. Small remaining fraction of H2S is removed with ZnO guard bed prior to methanation sector. However, CO2 stripped from amine unit also need to be cleaned from H2S before venting due to emission regulation. The difference is that in alternative schemes there is more choices available for that purpose. One of the examples is active carbon for H2S removal which requires oxygen present can be used.

**Thiophene removal:**
In the reference case thiophene is being converted to H2S in HDS reactor, while in all alternative schemes it is being removed together with aromatics via scrubbing oil.
A.4. Aspen modelling

A.4.1 EB case

PFD in Aspen plus was divided in sections. Overall schemes and PFD of individual sections are given below. Stream results are given in the subsequent tables.

Figure 22: Overall Aspen model

Figure 23: PFD section 2; EB reactor & separation section

Figure 24: PFD section 1; water scrubbing
Figure 25: PFD Section 5; Methanation

Figure 26: PFD Section 3; Sour-WGS

Figure 27: PFD Section 4; Amine scrubbing
### Table 12: Stream results; EB case; Sections 3 & 4

<table>
<thead>
<tr>
<th>SECTION 3</th>
<th>SECTION 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 HEX1-OUT</td>
<td>R1-IN</td>
</tr>
<tr>
<td>4 CO2</td>
<td>SA</td>
</tr>
</tbody>
</table>

| Temperature C | 60 | 250 | 249.2 | 429.7 | 70 | A | 70 | 20 | 46.8 | 250 | 70 | 70 | 70 | 70 |
| Pressure bar | 6.3 | 6.3 | 5.8 | 5.3 | 5.3 | 5.3 | 1 | 5.9 | 5.8 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 |
| Vapor Frac | 0.991 | 1 | 1 | 1 | 0.782 | 1 | 0 | 1 | 0.1 | 0 | 1 | 0.1 | 0.1 | 0 |
| Solid Frac | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Mole Flow kmol/hr | 700.893 | 700.893 | 784.012 | 1831.78 | 2381.18 | 2381.18 | 1916.55 | 1651.496 | 4053.044 | 8704.54 | 8704.54 | 1916.55 | 11319.99 | 7854.56 | 620.625 | 7584.944 |
| Mass Flow kg/hr | 15112.64 | 15112.64 | 2381.18 | 2381.18 | 1916.55 | 4651.496 | 4053.044 | 8704.54 | 8704.54 | 1916.55 | 11319.99 | 7854.56 | 620.625 | 7584.944 |
| Volume Flow l/min | 50824.59 | 80796.69 | 14719.13 | 21728.84 | 82694.89 | 82690.91 | 84.26 | 69978 | 154.02 | 59280.46 | 82690.91 | 22703.68 | 58515.23 | 4722 | 58510.51 |
| Enthalpy kcal | 2.1E+07 | 2E+07 | -4.7E+07 | -4.7E+07 | -3.6E+07 | -1.8E+07 | -1.6E+07 | -3.6E+07 | -2.7E+07 | -3.6E+07 | -2.4E+07 | -1.2E+07 | -984560 | -1.1E+07 |

### Table 13: Stream results; EB case; Section 5

<table>
<thead>
<tr>
<th>SECTION 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-IN</td>
</tr>
<tr>
<td>Temperature C</td>
</tr>
<tr>
<td>Pressure bar</td>
</tr>
<tr>
<td>Vapor Frac</td>
</tr>
<tr>
<td>Solid Frac</td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
</tr>
<tr>
<td>Mass Flow kg/hr</td>
</tr>
<tr>
<td>Volume Flow l/min</td>
</tr>
<tr>
<td>Enthalpy kcal</td>
</tr>
<tr>
<td>QVALNET MJ/kg</td>
</tr>
</tbody>
</table>
Figure 28: Cumulative Duty; EB case; PINCH=10C

Figure 29: Heat integration area; EB case
A.4.2 DEA case

The overall scheme for both of the DEA cases is given below. Section 1, 3, 4 and 5 are identical as in previous EB case (see A.4.1). Therefore, only PFD of section 2 is given.

Figure 30: Overall scheme; DEA case

Figure 31: Section 2; DEA case; DEA reactor & aromatics removal
### Table 18: Stream results; DEA-2 case; Overall

<table>
<thead>
<tr>
<th>Temperature C</th>
<th>OLGA-GAS</th>
<th>2</th>
<th>AROM</th>
<th>3</th>
<th>WATER</th>
<th>4</th>
<th>CO2</th>
<th>5</th>
<th>WASTE &amp; SNG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure bar</td>
<td>1</td>
<td>1</td>
<td>6.4</td>
<td>6.4</td>
<td>1</td>
<td>5.8</td>
<td>5.8</td>
<td>5.8</td>
<td>5.8</td>
</tr>
<tr>
<td>Membrane Flux</td>
<td>1</td>
<td>0.999</td>
<td>0.983</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Solid Flux</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mass Flow kg/hr</td>
<td>24698.77</td>
<td>17041.53</td>
<td>1437.651</td>
<td>1596.36</td>
<td>3888.579</td>
<td>3984.665</td>
<td>11314.98</td>
<td>7931.569</td>
<td>3112.189</td>
</tr>
<tr>
<td>Volume Flow l/min</td>
<td>505480.527</td>
<td>318395</td>
<td>28.57</td>
<td>52317.98</td>
<td>67.138</td>
<td>75102.22</td>
<td>20688.635</td>
<td>5562.769</td>
<td>54.278</td>
</tr>
<tr>
<td>Enthalpy kcal/hr</td>
<td>-44771000</td>
<td>-2.1E+07</td>
<td>117071.8</td>
<td>-2.2E+07</td>
<td>-1.5E+07</td>
<td>3.6E+07</td>
<td>2.4E+07</td>
<td>1.6E+07</td>
<td>-1.1E+07</td>
</tr>
</tbody>
</table>

### Table 19: Stream results; DEA-2 case; Section 1&2

<table>
<thead>
<tr>
<th>Temperature C</th>
<th>HEX1-IN</th>
<th>HEX1-OUT</th>
<th>1V</th>
<th>1L</th>
<th>NH3+HCL</th>
<th>2</th>
<th>2</th>
<th>CI-OUT</th>
<th>R-IN</th>
<th>R-OUT</th>
<th>BTX-FEED</th>
<th>BTX-L</th>
<th>BTX-V</th>
<th>AC-ADS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure bar</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Vacuum</td>
<td>0.014</td>
<td>0.018</td>
<td>0</td>
<td>0</td>
<td>0.015</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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<td>0.01</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
<td>1183.329</td>
<td>1183.329</td>
<td>760.061</td>
<td>423.268</td>
<td>1.716</td>
<td>758.346</td>
<td>758.346</td>
<td>758.346</td>
<td>758.346</td>
<td>755.442</td>
<td>755.442</td>
<td>16.187</td>
<td>739.254</td>
<td>0.095</td>
</tr>
<tr>
<td>Mass Flow kg/hr</td>
<td>24698.77</td>
<td>24698.77</td>
<td>17011.86</td>
<td>7626.913</td>
<td>30.325</td>
<td>17041.53</td>
<td>17041.53</td>
<td>17041.53</td>
<td>17041.53</td>
<td>17041.53</td>
<td>17041.53</td>
<td>1437.651</td>
<td>15603.88</td>
<td>7.525</td>
</tr>
<tr>
<td>Volume Flow l/min</td>
<td>505480.527</td>
<td>318395</td>
<td>28.57</td>
<td>52317.98</td>
<td>67.138</td>
<td>75102.22</td>
<td>20688.635</td>
<td>5562.769</td>
<td>54.278</td>
<td>1637.656</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enthalpy kcal/hr</td>
<td>-4.5E+07</td>
<td>-5.6E+07</td>
<td>-2.1E+07</td>
<td>-2.0E+07</td>
<td>-9.36644</td>
<td>-2.1E+07</td>
<td>-2.1E+07</td>
<td>-2.1E+07</td>
<td>-1.9E+07</td>
<td>-1.9E+07</td>
<td>-1.9E+07</td>
<td>-1.9E+07</td>
<td>-1.9E+07</td>
<td>-6.4</td>
</tr>
</tbody>
</table>

### Chart

1. OLGA-GAS 2 AROM 3 WATER 4 CO2 5 WASTE & SNG
2. SECTION-1
3. SECTION-2

### Footnotes

1. PPM: Parts per Million
2. PPB: Parts per Billion
3. Trace: Below detection limit
4. AC-ADS: Adsorption Column
5. BTX-FEED: Benzene, Toluene, Xylenes Feed
6. BTX-L: Benzene, Toluene, Xylenes Liquid
A.4.5 HEAT integration (DEA-1case, DEA-2 case)

Figure 32: Cumulative heat duty; DEA-1 case; PINCH=10C

Figure 33: Cumulative heat duty; DEA-2 case; PINCH=10C

Figure 34: Heat integration area; DEA case
A.5. Economic evaluation

A.5.1 Influence of differences in ethylbenzene and benzene prices

Figure 35: Influence of benzene and ethylene on price of styrene

Figure 36: Influence of ethylbenzene to benzene price difference to production cost of SNG
A.5.2 Influence of biomass price

Figure 37: Influence of co-products prices on production costs of SNG; Biomass=5$/GJ

Figure 38: Influence of co-products prices on production costs of SNG; Biomass=7.5 $/GJ

Figure 39: Influence of co-products prices on production costs of SNG; Biomass=10 $/GJ
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