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PO Box 117  
221 00 Lund  
+46 46-222 00 00

# Renewable gas in a Swedish context

LAURA MALEK | DEPARTMENT OF CHEMICAL ENGINEERING | LUND UNIVERSITY





# Renewable gas in a Swedish context

Laura Malek



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DOCTORAL DISSERTATION

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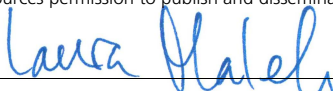
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Abstract <p>In order to increase the use of sustainable energy in Sweden, it is necessary to substitute fossil energy carriers with renewable counterparts. Synthetic natural gas (SNG) produced from renewable resources via biomass gasification and methanation could replace a proportion of the natural gas used in Sweden. In order to facilitate the implementation and expansion of SNG production and use in Sweden, development is necessary at multiple levels. In this thesis I have identified and investigated possible improvements for three different levels: national distribution, industrial production and specific plant improvements.</p> <p>There is a clear advantage in using the existing Swedish gas grid for the transportation and distribution of renewable gas. However, in order to inject renewable gas into the gas grid, strategies are required for handling gases of mixed qualities. An industry-wide task group was formed to develop guidelines for mixed quality gas for the Swedish gas grid, and Lund University and E.ON were assigned the task of drawing upon experience from other European countries to identify suitable strategies. Two strategies were identified: the flow-weighted heating value method and the state reconstruction tool. As a result of the work performed by the task group, the Swedish gas industry standard has been updated to include these two methods.</p> <p>By integrating biomass gasification and the SNG production process with an existing host plant, it is possible to reduce the investment and operating costs, compared to stand-alone production, while simultaneously exploiting synergistic effects by exchanging material and energy streams with the host plant. The majority of the integrated systems studied showed a system efficiency equal to those of stand-alone plants. The estimated SNG production cost for integrated cases is sufficiently low to compete with the cost of natural gas to household consumers, but not with the cost to commercial customers.</p> <p>It is imperative that SNG can be produced free from impurities in order to be approved for injection into the grid. Different aspects of gas cleaning technologies for tar and ammonia removal were studied. First, a proof-of-concept regenerative reverse-flow reactor was constructed for thermal cracking of tars. This method showed the ability to crack tar compounds and has the potential to be a highly efficient process step in a biomass gasification gas-cleaning train. Secondly, the possibility of regenerating the spent scrubber liquid used for tar removal in gasification plants, via centrifugation, was studied in order to improve the process economy. The results showed that centrifugation is a suitable method for removing heavy insoluble tars from the scrubber liquid, thus extending its lifetime considerably. Lastly, the possibility of removing ammonia by reaction with nitrous oxides over a vanadium-based or zeolite catalyst was investigated. Neither of these catalysts was deemed suitable due to either poor conversion or deactivation of the catalyst over time.</p> <p>From the results of these studies, it was concluded that the current outlook for Swedish SNG production by biomass gasification is not very promising. As natural gas in Sweden is used mainly as a fuel for industrial heat and power production, producing renewable SNG from biomass would appear to be a wasteful detour compared to the direct combustion of the biomass. This is especially true as the production of SNG is currently not sufficiently efficient for SNG to be produced at a cost that is competitive with that of natural gas. Transforming biomass into a useful vehicle fuel would be a far better use of renewable resources. However, clear regulations regarding the end use of renewable SNG would then have to be developed.</p>		
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Laura Malek



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*“To achieve great things, two things are needed;  
a plan, and not quite enough time”*

Leonard Bernstein



## Abstract

In order to increase the use of sustainable energy in Sweden, it is necessary to substitute fossil energy carriers with renewable counterparts. Synthetic natural gas (SNG) produced from renewable resources via biomass gasification and methanation could replace a proportion of the natural gas used in Sweden. In order to facilitate the implementation and expansion of SNG production and use in Sweden, development is necessary at multiple levels. In this thesis I have identified and investigated possible improvements for three different levels: national distribution, industrial production and specific plant improvements.

There is a clear advantage in using the existing Swedish gas grid for the transportation and distribution of renewable gas. However, in order to inject renewable gas into the gas grid, strategies are required for handling gases of mixed qualities. An industry-wide task group was formed to develop guidelines for mixed quality gas for the Swedish gas grid, and Lund University and E.ON were assigned the task of drawing upon experience from other European countries to identify suitable strategies. Two strategies were identified: the flow-weighted heating value method and the state reconstruction tool. As a result of the work performed by the task group, the Swedish gas industry standard has been updated to include these two methods.

By integrating biomass gasification and the SNG production process with an existing host plant, it is possible to reduce the investment and operating costs, compared to stand-alone production, while simultaneously exploiting synergistic effects by exchanging material and energy streams with the host plant. The majority of the integrated systems studied showed a system efficiency equal to those of stand-alone plants. The estimated SNG production cost for integrated cases is sufficiently low to compete with the cost of natural gas to household consumers, but not with the cost to commercial customers.

It is imperative that SNG can be produced free from impurities in order to be approved for injection into the grid. Different aspects of gas cleaning technologies for tar and ammonia removal were studied. First, a proof-of-concept regenerative reverse-flow reactor was constructed for thermal cracking of tars. This method showed the ability to crack tar compounds and has the potential to be a highly efficient process step in a biomass gasification gas-cleaning train. Secondly, the possibility of regenerating the spent scrubber liquid used for tar removal in gasification plants, via centrifugation, was studied in order to improve the process economy. The results showed that centrifugation is a suitable method for removing heavy insoluble tars from the scrubber liquid, thus extending its lifetime considerably. Lastly, the possibility of removing ammonia by reaction with nitrous oxides over a vanadium-based or zeolite catalyst was



investigated. Neither of these catalysts was deemed suitable due to either poor conversion or deactivation of the catalyst over time.

From the results of these studies, it was concluded that the current outlook for Swedish SNG production by biomass gasification is not very promising. As natural gas in Sweden is used mainly as a fuel for industrial heat and power production, producing renewable SNG from biomass would appear to be a wasteful detour compared to the direct combustion of the biomass. This is especially true as the production of SNG is currently not sufficiently efficient for SNG to be produced at a cost that is competitive with that of natural gas. Transforming biomass into a useful vehicle fuel would be a far better use of renewable resources. However, clear regulations regarding the end use of renewable SNG would then have to be developed.

# Populärvetenskaplig sammanfattning

Vårt samhälle letar ständigt nya vägar för att framställa förnybar energi från naturen för att minska vårt beroende av fossila bränslen. Vind- och solenergi är två vanliga exempel på förnybar energi. Utöver dessa två alternativ finns även möjligheten att omvandla olika sorters biomassa till förnybara bränslen som kan ersätta de fossila bränslen som vi använder idag. I Sverige, som till två tredjedelar är täckt av skog, ligger det nära till hands att utforska hur trä kan användas för svensk bränsleproduktion. I denna avhandling utforskas speciellt möjligheten att omvandla trä till förnybar metan vilken kan ersätta naturgas. För att utöka produktionen och användningen av förnybar metan i Sverige krävs forskning och framsteg på flera olika nivåer, från hur gasen skall distribueras nationellt till vilka förbättringar som kan göras på enskilda produktionsanläggningar. I denna avhandling har jag identifierat och utlett olika alternativ till förbättringar på tre olika nivåer: nationell distribution, industriell produktion och specifika produktions anläggningar.

Trä kan med olika metoder sönderdelas till mindre beståndsdelar och den mest välkända metoden är förbränning där trä omvandlas till vatten, koldioxid och värme. Genom att istället värma upp träet utan att förbränna det, en process som kallas förgasning, kan man utvinna en energirik gasblandning bestående av vätgas, kolmonoxid, koldioxid och lite metan. Denna gasblandning kan därefter via en rad kemiska reaktioner vidare omvandlas till ren metan som kan distribueras till olika industriella anläggningar, tankstationer och hushåll.

Sverige har ett naturgasnät som även kan användas för att transportera och distribuera förnybar gas. För att detta skall vara möjligt krävs dock metoder för att beräkna hur energivärdet i gasen förändras då naturgas och förnybar metan blandas. Ett korrekt fastställt energivärde är nödvändigt för att kunder som handlar gas från nätet inte skall feldebiteras. Genom att konsultera regelverk för gasnät från europeiska länder där blandning av gaser sker regelbundet (exempelvis Danmark, Nederländerna och Tyskland) identifierades två beräkningsmetoder, flödesviktning och quality tracking, vilka kan användas för beräkning av energivärde i det svenska gasnätet.

Förgasning av biomassa och produktion av förnybar metan sker oftast i enskilda industriella anläggningar. Dock finns tillfällen då andra befintliga industriella anläggningar antingen har ett överskott av biomassa, eller ett behov av metan, i sin process. Exempel på sådana anläggningar är pappersmassabruk eller sågverk där bark och trärester finns tillgängligt. Genom att integrera biomassaförgasning och metanproduktion med dessa anläggningar går det att utbyta både material och energi mellan anläggningarna. Detta kan leda till minskade kostnader för framställandet av metan och bättre utnyttjande av restprodukter från andra anläggningar. Ett antal hypotetiska fall av integrerade anläggningar studerades och resultaten visade att metan

kan produceras till ett pris som är konkurrenskraftigt gentemot naturgas som säljs till enskilda hushåll, men inte jämfört med priserna som gäller för industrin.

Det pågår ständig forskning och utveckling för att förbättra olika delar av förgasningsprocessen och metanproduktionen. En viktig aspekt är att utveckla effektiva tekniker för att rena gasblandningen som erhålls vid förgasning från olika föroreningar. Detta är nödvändigt för att kunna producera metan som möter de kvalitetskrav ställs på gas som skall matas in på gasnätet. Dessutom kan förbättring av olika reningstekniker bidra till sänkta driftskostnader vilket möjliggör produktion av förnybar metan till ett lägre pris. I denna avhandling har olika aspekter av tekniker för omvandling och fysiskt avlägsnande av tjära och ammoniak, två vanliga föroreningar som bildas vid förgasning av biomassa, studerats.

Framtiden för produktion av förnybar metan från biomassa i Sverige är i dagsläget mycket oviss. Detta beror till största delen av att den höga produktionskostnaden gör att den förnybara metanen inte är tillräckligt konkurrenskraftig för att kunna säljas till industriella anläggningar. Ett bättre alternativ skulle vara att sälja den förnybara metanen som fordonsbränsle. Detta kräver dock riktade direktiv om hur gasen får användas, direktiv som för närvarande saknas.

## List of Publications

This thesis is based on the following five papers, which will be referred to in the text by their Roman numerals.

- I. **Malek, L** & Hulteberg, C. “Measuring and Ensuring the Gas Quality of the Swedish Gas Grid”, Report No. 2016:325, Energiforsk (2016)
- II. **Malek, L**, Tunå, P & Hulteberg, C. “Industrially Integrated Gasifiers for Biochemical and Biofuel Production: A Meta-Analysis”, Manuscript
- III. Tunå, P, Bauer, F, Hulteberg, C & **Malek, L**. “Regenerative Reverse-Flow Reactor System for Cracking of Producer Gas Tars”, Biomass Conversion and Biorefinery (2013)
- IV. **Malek, L**, Hulteberg, C & Svensson, H. “Scrubber Liquid Recovery in Biomass Gasification Plants: Centrifugation as a Method for Tar Separation”, Biomass Conversion and Biorefinery (2016)
- V. **Malek, L**, Tunå, P & Hulteberg, C. “Catalytic Abatement of NH<sub>3</sub> using NO<sub>x</sub> in Reducing Environment”, Topics in Catalysis (2015)

## Author contributions

- I. Measuring and Ensuring the Gas Quality of the Swedish Gas Grid  
I planned the study and performed most of the work. I wrote the manuscript together with my co-author.
- II. Industrially Integrated Gasifiers for Biochemical and Biofuel Production: A Meta-Analysis  
I participated in the planning of the study and performed most of the data gathering and analysis. I wrote the manuscript together with my co-authors.
- III. Regenerative Reverse-Flow Reactor System for Cracking of Producer Gas Tars  
I participated in the experimental work and was responsible for the tar analysis. I wrote a section of the manuscript.
- IV. Scrubber Liquid Recovery in Biomass Gasification Plants: Centrifugation as a Method for Tar Separation  
I planned the study and performed all the experimental work. I wrote the manuscript.
- V. Catalytic Abatement of  $\text{NH}_3$  using  $\text{NO}_x$  in Reducing Environment  
I participated in the planning of the study and performed all the experimental work and analysis. I wrote the manuscript together with my co-authors.

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# 1

## Introduction

Various types of biomass are increasingly being regarded as viable, renewable feedstocks for the production of fuels and other products that are currently mainly or solely produced from fossil sources. Actors in the energy and industrial sector are gradually coming to the realization that the use of fossil feedstocks alone is unsustainable. Research is being carried out in various fields worldwide to identify new pathways and to develop the technologies needed to transform and refine biomass feedstocks such as wood, grass and algae into chemicals, fuels and electricity. Wood has always been an important raw material in Sweden, as about two thirds of the country is covered by forests. Refining wood into high-value products is by no means a novel idea. In his book, *The Coming Age of Wood* [1], Egon Glesinger gives an extensive review of the ways in which wood can be used to produce products as varied as fuels, plastics and food substitutes. Glesinger especially highlights the way in which various branches of the Swedish forestry industry combined to become an integrated and innovative production platform during World War II. The work described in this thesis explores part of Glesinger's vision by examining how Swedish forests can be used to produce renewable gas. The whole production chain, from the production of renewable gas to its distribution has been investigated.

The term “renewable gas” is used rather broadly, for a wide range of different compounds produced with different technologies. Biogas produced by anaerobic digestion, synthetic natural gas (SNG) by gasification and hydrogen formed by the electrolysis of water are examples of renewable gases. What differentiates renewable gases from fossil gas is that renewable gases are produced from renewable sources, such

as wood. In this thesis, the term renewable gas is used to describe SNG produced by biomass gasification.

## 1.1 Research questions

The aim of the research described in this thesis was to answer the overall question: “What measures are, and needs to be, taken to facilitate the implementation and expansion of SNG production and use in Sweden?”. As this question is rather broad, it was divided into the following specific research questions.

- How can the distribution of SNG be improved?
- Can SNG compete with natural gas?
- What are the challenges in individual production plants?
- Is there a future for SNG in Sweden?

To be able to answer these questions, research was performed on different levels, ranging from an aggregated, country perspective concerning gas distribution, down to a high degree of detail for specific problems in individual plants. Figure 1.1 illustrates the three different levels on which research was carried out, including the topics of the Papers, I-V.

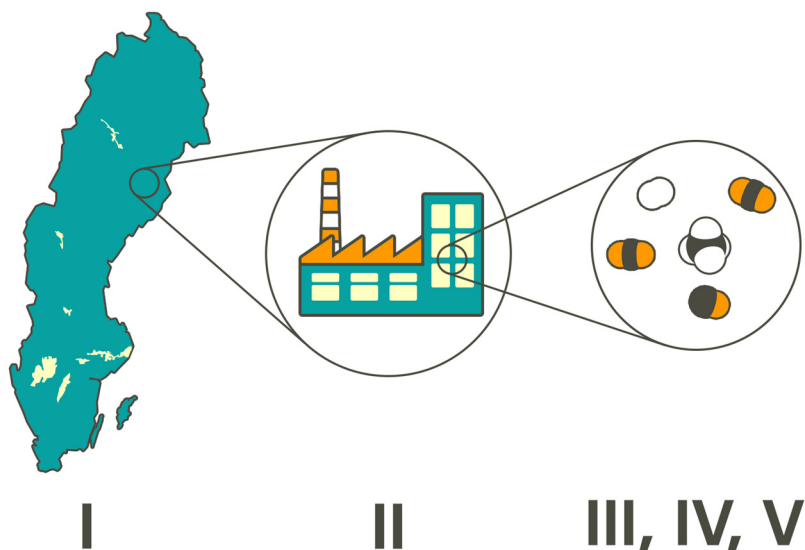


Figure 1.1. The three levels at which research was carried out: distribution, production and detail and the papers covering each level.

At the highest level, the options for distributing renewable gas throughout Sweden were examined, with special focus on ways in which renewable gas can be introduced into the Swedish gas grid. **Paper I**, *Measuring and Ensuring the Gas Quality of the Swedish Gas Grid*, describes methods for the calculation of heating value in gas grids with multiple injection points with mixed gas quality, in order to update the Swedish gas industry standard. The next level concerns industrial production, and the possibility of integrating biomass gasification for biofuel and chemical production in existing host industries, for example, pulp and paper mills, to exploit synergistic effects and increase revenue, and is presented in **Paper II**, *Industrially Integrated Gasifiers for Biochemical and Biofuel Production: A Meta-Analysis*. **Papers III, IV and V** each deal with different aspects of plant and gasification improvement, in particular the removal of impurities from the producer gas (see Section 2.3.2 for definition). In the study described in **Paper III**, *Regenerative Reverse-Flow Reactor System for Cracking of Producer Gas Tars*, a novel tar-cracking reactor for the removal of tar from producer gas was examined. The research on tar removal was continued by examining the possibility of recovering and reusing the scrubber liquid used for removal of tar from producer gas, and is described in **Paper IV**, *Scrubber Liquid Recovery in Biomass Gasification Plants: Centrifugation as a Method for Tar Separation*. Recovering and reusing the scrubber liquid reduces the operational cost of the plant, thus reducing the production cost. Finally, **Paper V**, *Catalytic Abatement of  $NH_3$  Using  $NO_x$  in Reducing Environment*, describes the removal of ammonia, another common impurity, from the producer gas using nitrous oxides.

## 1.2 Outline

A brief background describing renewable gas, and its production and distribution, is given in the next chapter, to provide the reader with the framework necessary to fully understand the work presented in this thesis. This is followed by three chapters dealing with the research questions defined above. Each chapter reflects one of the three research levels, starting with distribution, which is based on the research presented in **Paper I**, followed by industrial production, based on **Paper II**, and then specific plant improvements (**Papers III, IV and V**). Finally, the conclusions drawn from this work are presented together with suggestions for future research.





# 2

## SNG from biomass

The research presented in this thesis covers different aspects of SNG produced through biomass gasification, from biomass to gas distribution options. This chapter introduces the reader to the various stages of this process, starting with an explanation of what SNG is, which feedstocks are available, the concepts of gasification, gas cleaning and SNG synthesis, and finishing with the options available for gas distribution.

### 2.1 SNG

Synthetic natural gas, sometimes called substitute natural gas, is an energy gas consisting mainly of methane. Other methane rich energy gases are natural gas, landfill gas and biogas. These gases are similar but differ in method of production, gas composition and impurities present. Landfill gas is generated naturally at landfills by the microbial degradation of waste, however, it can also result from the evaporation of volatile organic compounds or chemical reactions between waste components [2]. Biogas is produced by the anaerobic digestion of organic waste such as agricultural waste, manure, sewage or food waste. The term SNG is used for methane synthesized chemically from hydrogen and carbon oxides, a process known as methanation [3,4]. The reactant gas can be produced from various feedstocks, either fossil (coal, oil shale) or renewable (biomass, electrolysis of water). Whereas natural gas is a fossil fuel, SNG from renewable sources, landfill gas and biogas are considered renewable fuels.

## 2.2 Feedstock

Any carbonaceous fuel, from fossil or renewable sources, can be used as a feedstock in the gasification process [5]. The composition and properties of the feedstock are of great importance for both the performance of the gasification process, as well as the composition of the gas and the levels of impurities exiting the gasifier.

Woody biomass consists mainly of cellulose, hemicellulose, lignin and minerals [6]. The exact composition varies, not only between different species, but also within the species depending on age and which part of the plant is considered. Recycled wood and forest residues may also contain contaminants in the form of chemicals and soil. The gasification of wood pellets will thus generate a different gas from the gasification of bark, forest residues or recycled wood. Recycled feedstocks and feedstocks with high lignin and mineral contents are often considered low-value raw materials, and are therefore generally cheaper to acquire than feedstocks rich in cellulose and hemicellulose, as can be seen in Table 2.1. However, alkali metals present in the biomass (i.e. Na, K, Mg, P, Ca) can form corrosive compounds and are known to react with silica to form alkali silicates, which cause fouling of the equipment [6,7]. While the inherent silica content in the biomass can be low, additional silica may be introduced in the form of soil during collection, for example, of forest residues. This can increase the total silica content significantly and may lead to operational difficulties. Lignin has a very rigid structure as it consists of large aromatic complexes, making it difficult to decompose, and a high lignin content may thus lead to a lower conversion efficiency [8]. Although the lower price of low-quality feedstocks makes them interesting for use in conversion processes, the additional strain on the process, and the possible reduction in product yield must also be considered.

**Table 2.1 Swedish prices for various woody feedstocks [9]**

<b>Fuel type</b>	<b>Price (SEK/MWh)</b>
Densified wood fuels (incl. pellets)	282
Forest residues	187-195
Recycled wood	90
Solid by-products (incl. sawdust, bark)	164-165

## 2.3 Production process

The process of converting biomass into SNG is described in four subsections, each focusing on a specific part of the process: biomass pre-treatment, gasification, gas cleaning and SNG synthesis and upgrading. All four steps are vital in order to produce a high-quality product.

### 2.3.1 Pre-treatment

Prior to gasification, the biomass is subjected to various pre-treatment steps. Depending on the state of the raw biomass, it may be necessary to dry, chip and/or grind it. The steps required also depend on the gasification technology applied (see Section 2.3.2). Size reduction can be a highly energy-intensive process as the energy required by chippers and grinders is proportional to the reduction in size of the feedstock [10]. This means that gasification technologies that require fine-particle biomass will have higher operational costs than those using courser material.

The next step in pre-treatment is to dry the biomass. Raw biomass has a moisture content of about 50 wt% and should be dried to a moisture content of 10-20 wt% before gasification, as using high-value heat in the gasifier for water evaporation leads to a higher energy demand [10].

### 2.3.2 Gasification

Biomass gasification is a thermochemical process in which biomass is converted into a gaseous product using an oxidizing agent (air, oxygen or steam). Heat is provided to the process by combusting a fraction of the biomass. The gas leaving the gasifier consists mainly of carbon dioxide, carbon monoxide, methane and hydrogen. The exact composition of this gas varies depending on various process aspects, such as the gasification technology, feedstock, oxidizing agent and operating conditions. This gas is referred to as *producer gas* throughout this thesis.

A wide range of gasifier designs is currently in use. However, the majority can be grouped into one of three main categories, based on the mode of contact between the solids and the gasifying medium: fixed-bed, fluidized-bed and entrained-flow gasifiers [5,10]. Each type of gasification technique has advantages and disadvantages, making them suitable for use on different scales, as illustrated in Figure 2.1.

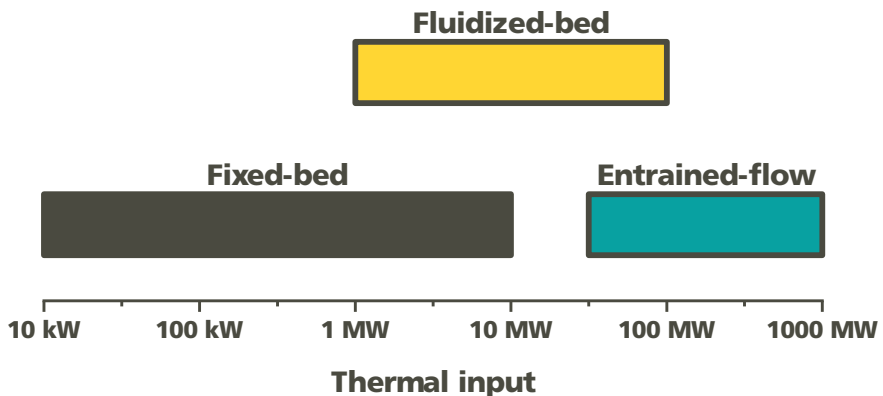


Figure 2.1 Range of applicability of various types of biomass gasifiers.

In fixed-bed gasifiers (also known as moving-bed), the biomass is placed on top of a grate inside the gasifier. The height of the bed is reduced as the material is gasified. The simple design of these gasifiers means that construction is inexpensive, and the use of extremely inhomogeneous feedstock is possible. However, as heat transfer within the bed is rather poor, it is difficult to achieve uniform temperature and gas composition gradients across the gasifier when scaling up the process. This leads to reduced gasification efficiency and increased tar production [10].

Fluidized-bed gasifiers are filled with inert or catalytically active sand, alumina or another mineral, which is fluidized using the oxidizing agent [11]. This helps break up and distribute the biomass, ensuring good mixing and temperature uniformity throughout the gasifier, leading to high conversion rates and low tar content. Although the technology can be used with a wide range of fuel particle sizes, the requirement on the size of the feedstock is stricter than in fixed-bed gasifiers, as it must be possible to fluidize the feedstock. A special variant of fluidized-bed gasifiers are indirectly heated gasifiers, which consist of two twin reactors with the bed material circulating between them. The bed material is heated in a combustion chamber, using air as fluidizer, and is then carried over to the gasification chamber fluidized by steam. It is thus possible to create a nitrogen-free producer gas without using pure oxygen as the oxidizing agent, reducing both investment and operating costs, as an air separation unit is no longer needed [12].

Entrained-flow gasifiers can be operated with feedstocks in solid, liquid or slurry form, which makes them very versatile [12]. In addition, they can be operated at temperatures high enough to approach conversions of 100% while producing a relatively tar-free producer gas. However, in order for the feedstock to be entrained in the reactor by the oxidizing agent it has to be finely ground, leading to increased pre-treatment, and thus operating, costs.

### 2.3.3 Gas cleaning

The producer gas leaving the gasifier contains contaminants in the form of particles, tar, alkali, nitrogen compounds, halogens and sulphur compounds, all of which must be removed prior to the SNG synthesis stage, as they can cause complications such as blockage of equipment or deactivation of catalysts.

The particulate matter in the gas is a combination of ash, unconverted carbonaceous fuel and, in the case of fluidized-bed gasification, bed material. The particles are deposited on surfaces in the equipment and cause blocking if they are not removed from the gas [13]. Cyclones are often used in the first removal step. However, due to the small size of the particles, filters are often added as a secondary step. Alternatively, the fine particles can be removed in a scrubber together with the tar.

The tar consists mainly of aromatic organic compounds that are formed during gasification [14]. Figure 2.2 shows four examples of tar compounds specifically chosen to illustrate the diversity in the size and type of ring structures found among tars. It should be noted that these examples represent only a small selection among hundreds. When the producer gas is cooled the tars start to condense, causing severe blocking of the equipment. Common methods of tar removal are mechanical removal, using scrubbers or filters, or conversion of the tars using thermal or catalytic cracking [13,15].

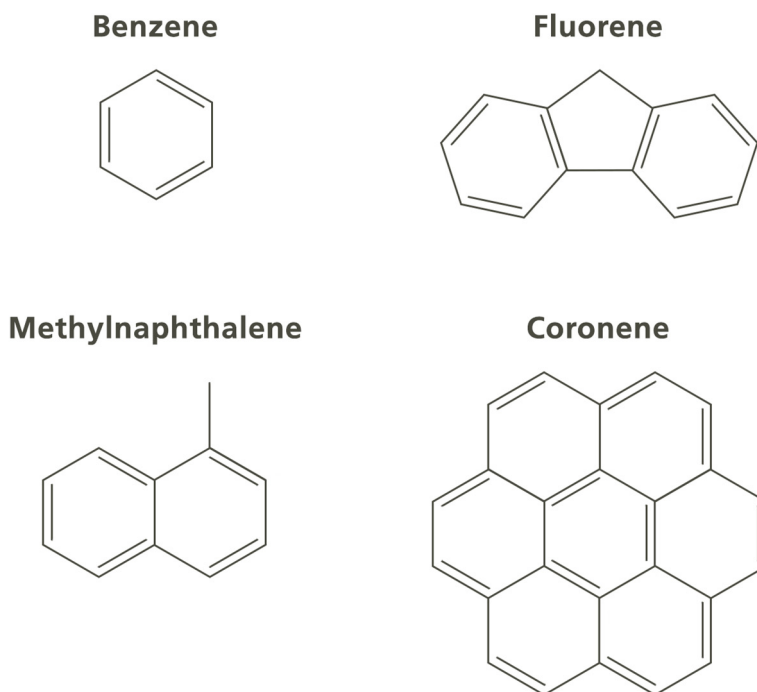


Figure 2.2 Examples of tar compounds illustrating the range of tars found in producer gas.

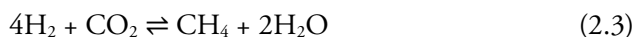
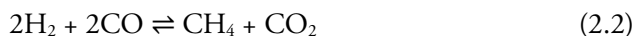
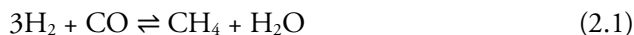
Alkali, halogens and sulphur compounds are removed by chemical reactions with different sorbents [15]. Both alkali and sulphur compounds cause catalyst poisoning, and must thus be removed prior to synthesis, while halide gases tend to be converted into acids (e.g. HCl), leading to corrosion of downstream equipment [13].

Nitrous compounds (e.g.,  $\text{NH}_3$ ) may poison some catalysts, however, the main concern is the formation of nitrous oxides upon combustion. As nitrous compounds are highly soluble in water, water scrubbing is commonly used in industry. It is also possible to decompose nitrous compounds using various catalysts, where nickel catalysts have proven to be the most successful [16].



### 2.3.4 SNG synthesis and upgrading

Methanation is a heterogeneously catalysed process; nickel catalysts being the most commonly used in industry [3,4]. Methane can be formed by methanation of either carbon monoxide (reaction 2.1) or carbon dioxide (reactions 2.2-2.3).



For reaction 2.1 to be active and to achieve good CO conversion, the stoichiometric H<sub>2</sub>/CO ratio must be at least 3. However, the H<sub>2</sub>/CO ratio in producer gas is usually below 2. The ratio can be adjusted prior to methanation using the water-gas shift reaction (reaction 2.4), which also occurs naturally in the presence of a nickel catalyst. Several technologies for both carbon monoxide and carbon dioxide methanation are commercially available. For example, the TREMP technology developed by Haldor Topsøe was used in the Swedish GoBiGas gasification plant [17]. Finally, in order for the SNG to meet the requirements for grid injection, the remaining CO<sub>2</sub> in the gas must be removed, a process known as gas upgrading. Several gas-upgrading technologies are commercially available, examples of which are amine scrubbing, membrane separation and pressure swing adsorption [18].

## 2.4 Gas distribution

Gas can be transported and distributed in Sweden today via a national gas grid, or by road, either as compressed biogas (CBG) or liquefied biogas (LBG) [9,19,20].

Before SNG can be injected into the Swedish gas grid, the quality of the gas must be adjusted to meet the requirements of the Swedish vehicle fuel regulations. SNG generally has a lower energy content than specified in the regulations, and propane is therefore added to the gas to increase its energy content. The same applies to CBG and LBG. A major advantage of grid distribution is that the transportation cost is not directly dependent on the transportation distance. However, this only applies for already existing grids. The capital cost of constructing new gas grid infrastructure is between 700 and 1500 SEK/m, depending on the type of grid [19].

CBG is transported in gas bottles in swap bodies that can be transported by truck to the consumer [19]. Each truck has the capacity to transport 4500 Nm<sup>3</sup> of CBG at a time. This form of transport is highly flexible, as large numbers of trucks are available, and there is no dependence on an existing gas grid infrastructure [9]. Additionally, the

initial investment cost of the equipment needed to compress the gas is relatively low. However, in contrast to transportation by a gas grid, the cost of road transport increases linearly with the transportation distance, making road transportation over long distances prohibitively expensive. If long transportation by road is necessary, LBG should be used instead of CBG. LBG is produced by cooling the methane below its boiling point of  $-162\text{ }^{\circ}\text{C}$  at atmospheric pressure [19]. The initial investment cost for the liquefaction facility is significantly higher than that of the compression equipment needed for CBG production. Large production volumes are thus needed for the investment to be viable. The greatest advantages of LBG over CBG are that larger quantities of gas can be transported due to it being liquefied, and the energy content per unit volume of LBG is 2.6 times greater than that of CBG at 200 bar. This makes LBG more competitive over longer distances.

Of the options discussed above, transportation by gas grid is the most energy efficient and environmentally friendly, and should be used when possible. However, if the SNG production plant is not located in the vicinity of a gas grid it will be necessary to use two road transport.



# 3

## Distribution options

As mentioned in the previous chapter, the main options for the distribution of SNG are gas grids and road transport. Aspects such as the location of the production plant and the consumer, gas production volume and consumption volume, available infrastructure and intended use of the gas all play a part in the choice of the most appropriate transport and/or distribution system. According to Hjort and Tamm, pipelines are the most economical alternative for both transporting and distributing gas, provided the gasification plant is located within 30 km of a local gas distribution grid [19]. SNG produced at plants not situated close to a gas grid can instead be transported as CBG or LNG using trucks. However, due to the favourable economics associated with pipeline transport, SNG production plants built close to either the Swedish transmission grid or a regional distribution grid would have a clear advantage [9].

Consumers connected to the Swedish gas grid rely on the ability of the grid to provide a constant supply of gas with a high and consistent quality. Historically, the Swedish transmission grid has mainly been supplied with a steady, relatively consistent supply of Danish North Sea gas via a single injection point at Klagshamn, south of Malmö. This has ensured a relatively uniform gas quality throughout the entire transmission grid and regional distribution grids. However, this scenario is gradually changing, as higher fluctuations in gas quality can be expected as increasing amounts of German gas reach Sweden via the Danish gas grid [21,22]. The causes of these fluctuations are described in Section 3.1. Nationally, increasing amounts of renewable gas are being injected into both the transmission grid and directly into various regional distribution grids (Figure 3.1), which also contributes to fluctuations in gas quality. For example,

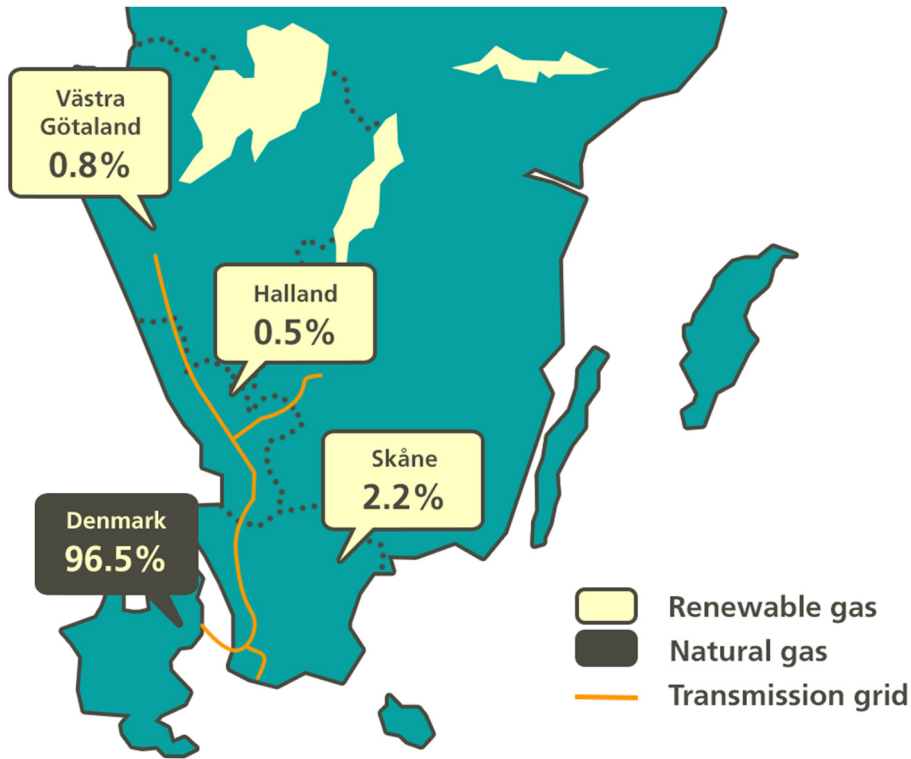


Figure 3.1 Shares of renewable and natural gas injected into the Swedish gas grid by region during 2016 [24]. Distribution grids are not shown.

the production of 120 GWh biogas per year by anaerobic digestion at Sweden’s largest biogas plant at Jordberga, outside Trelleborg, will affect the gas quality in the distribution grid in this region. In addition to the injection points in Klagshamn and Jordberga, about 10 other anaerobic digestion plants deliver biogas to regional distribution grids in Sweden [21]. The GoBiGas plant in Gothenburg was projected to deliver 160 GWh of SNG annually to the transmission grid, which would have caused a significant variation in gas quality around Gothenburg. Unfortunately, the Board of Göteborg Energi (the owners of GoBiGas) decided to discontinue operation at GoBiGas until further notice due to the major financial strain placed on the company throughout the GoBiGas project [23]. Although this will affect the expansion of renewable SNG in Sweden, the production of renewable gas will continue to grow, and part of the gas produced will most likely be fed into the Swedish gas grid.

As the increasing amount of renewable gas being injected into the Swedish gas grid causes fluctuations in gas quality, it is necessary to monitor the gas quality in a more controlled and detailed way than previously required. It was thus recognized by the

Swedish gas industry that there was a need to update the national regulations on gas quality control to accommodate ongoing developments in the gas market. An industry-wide task group was formed, the members being appointed by Energigas Sverige, to undertake the task of proposing appropriate updates to the current regulations. Lund University in collaboration with E.ON took part in this process, and were assigned the task of drawing upon experience from other European countries with existing regulatory frameworks regarding mixed gas quality systems, as in contrast to the Swedish gas grid, the European gas network is highly inter-connected, with gas being provided from multiple production sites. Various European gas organizations were contacted, and regulatory and standard documents such as the Danish *Naturgasselskabernes kontrolmanual for allokering af brændværdi i distributionsnettet* [25], the German *Technische Regel Arbeitsblatt G 685* [26] and the ISO standard *Natural gas - Energy determination ISO 15112:2011* [27] were reviewed in order to gain valuable insight into regulations with possible relevance for the Swedish gas market.

**Paper I** presents the results of this review. The remainder of this chapter will be devoted to the findings regarding gas quality and mixed quality gas handling, as well as addressing how this research is related to the research questions stated in Chapter 1.

### 3.1 Gas quality

The term “gas quality” can have different meanings depending on the intended use of the gas. It can, for example, refer to the composition of the gas, the Wobbe index or the heating value, and which of these parameters is most important depends on the intended end use of the gas. Gas composition is of great importance in the chemical industry when the intended use is the synthesis of other products, while the heating value is the main concern in heating systems. As gas is mainly used for various heat and power applications in Sweden, the term “gas quality” will henceforth be used to refer to the higher heating value of the gas. The heating value of an energy gas is dependent on its composition, and the heating value of renewable gas thus differs from that of fossil natural gas, while the heating value of natural gas also differs depending on gas field origin. Table 3.1 gives the composition and heating value for natural gas from different countries in comparison to SNG.

Fossil natural gas contain higher hydrocarbons (i.e. ethane, propane, butane), which are not present in SNG. As a result, the heating value of SNG is about 5-10% lower than that of natural gas, as these higher hydrocarbons have a larger heating value than methane. It is this difference in gas composition that causes the heating value fluctuations when renewable gas is fed into the gas grid.

**Table 3.1. Gas composition (mol%) and higher heating value (HHV) for natural gas from different origins, biogas and SNG [21]**

	North Sea gas	German gas	Russian gas	Biogas (upgraded)	SNG
Methane	90.07	91.18	96.96	90.94	94.5-96.4
Ethane	5.68	4.62	1.37	-	-
Propane	2.19	0.95	0.45	5	-
Butane	0.90	0.29	0.15	-	-
Pentane +	0.28	0.1	0.03	0.5	-
Nitrogen	0.28	1.6	0.86	0.69	1.6-2.6
Carbon dioxide	0.6	1.26	0.18	2.68	0.5
Carbon monoxide	-	-	-	-	1-1.2
Hydrogen	-	-	-	-	2.0
HHV (kWh/Nm <sup>3</sup> )	12.1	11.4	11.2	11.6	10.7
HHV (MJ/Nm <sup>3</sup> )	43.7	41.02	40.3	41.9	38.5

### 3.2 Strategies for mixed gas quality handling

Two approaches can be used for handling systems where gas streams with different gas qualities are injected. The first is to circumvent the problem of injecting gas of lower quality into the grid by equilibrating the heating values of the gas streams. This can either be done by adding propane to lower-quality gas streams, a process known as propanation, or by reducing the heating value of higher-quality gas stream by diluting them with an inert gas, such as nitrogen. Propanation is the primary method used when injecting upgraded biogas into the Swedish gas grid [21]. However, adding propane to renewable gas increases the production cost. In addition, the propane currently used for propanation originates from fossil feedstocks, and its use is thus questionable in the concept of renewable gas. Another option is to inject such small amounts of renewable gas that the overall heating value of the gas in the grid is not significantly affected. This was done in Gothenburg, where small amounts of SNG produced by the GoBiGas plant were fed into the transmission grid.

The second approach that can be used in systems with gas quality mixing is to calculate and allocate one or more new heating values to the affected area. Two major methods found in the reviewed regulations were deemed to be highly interesting, namely the flow-weighted heating value method and the state reconstruction tool.

### 3.2.1 The flow-weighted heating value

Using this method, it is possible to assign a calculated heating value of the gas in a grid downstream of, or at a mixing point where, multiple gas streams of different gas quality meet. The method takes into account the heating values ( $H_{s,n}$ ) of the gas streams involved and the volumetric gas flow ( $Q_n$ ), and the resulting heating value, ( $H_s$ ) is calculated according to Eq. 3.1.

$$H_s = \frac{\sum_{i=1}^n H_{s,i} \cdot Q_i}{\sum_{i=1}^n Q_i} \quad (3.1)$$

This method can be used to assign a calculated heating value for an entire grid with good accuracy, in particular when the mixing of gases occurs before reaching the grid (see Figure 3.2a). On the other hand, if gases with significantly different heating values are to be mixed within a grid, then assigning one heating value for the gas in the entire grid will lead to overcharging of customers closest to the injection point. In the case of large differences between the heating values in the incoming gas streams, the grid should be divided into smaller zones, each with its own allocated heating value (see Figure 3.2b). Zones close to the injection points are then assigned the heating value of the incoming stream, while a flow-weighted heating value is calculated for the mixing

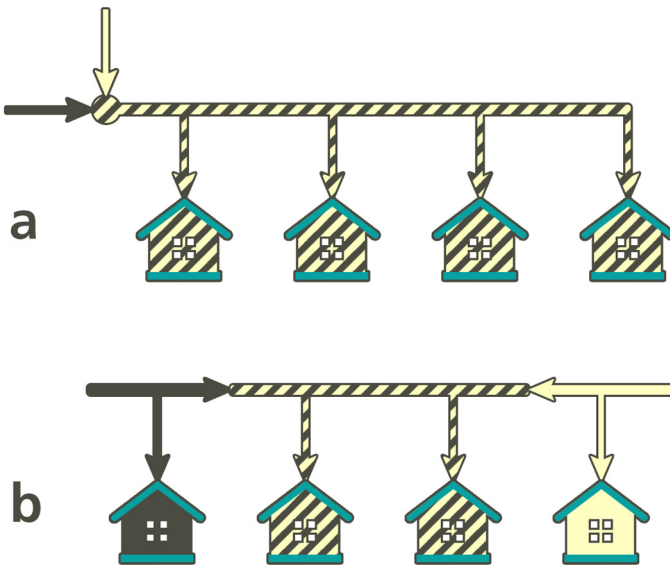


Figure 3.2 Mixing of gases (a) before reaching the grid: one heating value applies throughout the grid, (b) in the grid: multiple heating values apply.



zones. As presented above, the flow-weighted heating value method works well for simple grid configurations, but as grid complexity increases, so does the uncertainty in the allocated heating values, and thus the risk of incorrect debiting, as customers are receiving gas of another quality than that for which they are charged. For very complex grids with a high number of injection points or large variations in incoming heating value it is instead recommended that a state reconstruction tool be used instead (Section 3.2.2).

### 3.2.2 The state reconstruction tool

The task of allocating heating values in a distribution grid becomes increasingly complicated as the number of injection points increases. In very complex grid structures the accuracy of flow-weighted heating values decreases to a point where the correct debiting of customers can no longer be guaranteed. At this level of grid complexity a state reconstruction tool called a quality tracker can be implemented to correctly allocate heating values throughout the grid. With the help of a quality tracker, it is possible to simulate the affected grid based on topological data, heating values at entry points, and gas volume flows at both entry and exit points [28]. The simulation then allows the user to calculate the heating value at any point in the gas grid at any time. An example of a quality tracker gas grid simulation is shown in Figure 3.3. This specific simulation shows a simplified gas grid structure for the Lund-Staffanstorpe-Dalby gas grid in southern Sweden. Each gas injection point has been given a unique colour to better visualize gas mixing in the grid.

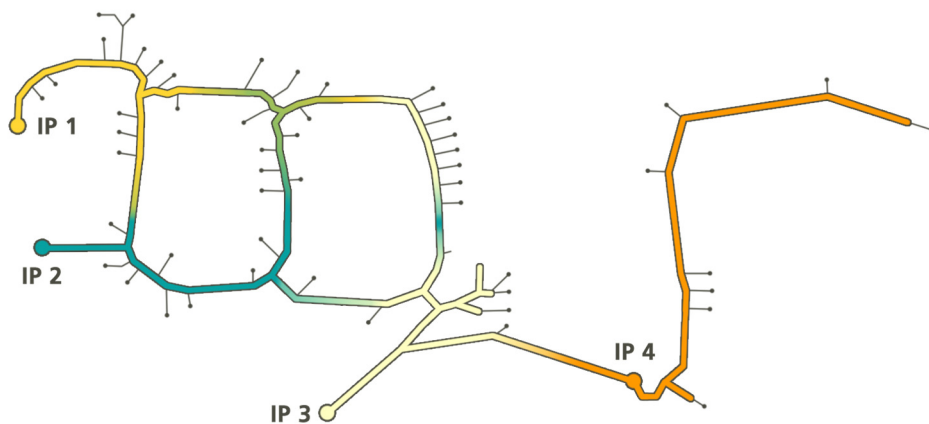


Figure 3.3 Quality tracking simulation of the Lund-Staffanstorpe-Dalby gas grid. Injection points (IP) have been marked with a coloured circle. The grey points mark outtake nodes. Adapted from [29].

### 3.3 The Swedish context

There is a clear advantage in using the existing infrastructure in the form of the Swedish gas grid for the transportation and distribution of renewable gas. The results presented in **Paper I** show that it is possible to add SNG to the grid without propanation if a heating value determination and allocation method, such as the flow-weighted heating value method or quality tracking, is applied. Although the flow-weighted heating value method is relatively simple and would probably be sufficiently accurate for many parts of the Swedish gas grid, it would still be advisable to implement a quality tracker to determine and monitor the heating values throughout the entire grid, as was recommended in **Paper I**. This would allow the gas grid to expand with less restrictions over time, and thus facilitate the inclusion of future SNG and biogas production plants of varying production capacities without risking hindrance due to increasing grid complexity. As a result of the work carried out in collaboration with E.ON, the Swedish gas industry standard, *Branschgemensamma metoder för bestämning av värmevärde* [30], has been updated to include the use of quality tracking, as well as requirements on the accuracy and control of heating values determined with a quality tracker. This has enabled quality tracking to be implemented by, for example, SWEDEGAS, which operates the Swedish transmission grid. In order to take advantage of the existing gas grid infrastructure, SNG production plants would have to be constructed relatively close to the grid in order to minimize the investment cost of additional pipeline infrastructure. In special cases, such as that discussed in Chapter 4, SNG might be produced at the site of existing industrial plants, which might not be located close to an existing gas grid. In such cases, other transportation options (road transport of CBG or LBG) must be considered.



# 4

## Industrial production

The second level discussed in this thesis concerns possible options for the set-up of a biomass gasification plant to produce SNG. There are three major approaches to process and plant: stand-alone production, plant co-location and gasifier integration. All have advantages and limitations, and are therefore suitable in different situations. Choosing a plant configuration that suits the prevailing conditions (such as local SNG demand, feedstock availability and existing distribution infrastructure) is necessary in order to minimize capital and operational costs, which is essential when producing a market competitive product.

It is common practice in many industries to build stand-alone plants, and the same applies to biomass gasification plants. Stand-alone SNG plants have an inherent flexibility as they can be built virtually anywhere, and can be scaled to meet, for example, an existing SNG demand or a certain biomass availability. However, stand-alone plants tend to have a rather high specific investment cost (cost per unit product) as certain equipment and process steps are necessary, regardless of the planned SNG production volume. Examples of such equipment and steps are biomass pre-treatment, producer gas clean-up train and SNG synthesis equipment. In addition, depending on the existing infrastructure available in the area surrounding the site of the plant, it might be necessary to develop infrastructure, such as biomass logistics or SNG distribution systems, further adding to the overall investment cost. Small-scale biomass gasification plants built to make use of small amounts of excess biomass, or to meet a small SNG demand, will therefore seldom be profitable. Economy-of-scale often plays an important role when planning new plants as investment costs do not scale linearly with plant size. One way to reduce the investment cost associated with infrastructure (and

transportation) is by co-locating the gasification plant with another industrial plant that either has a demand for SNG or excess biomass that is suitable for gasification. Figure 4.1 illustrates the difference between stand-alone, co-located and integrated gasification plants, the last of which will be discussed below.

The last approach to process and plant design is to go one step further from co-location and fully integrate biomass gasification and the SNG production process with an existing host plant. This configuration differs from co-location in the sense that biomass gasification is no longer viewed as a separate process but as a part of a host plant (Figure 4.1). The attractiveness of this configuration lies in the possibility of further reducing

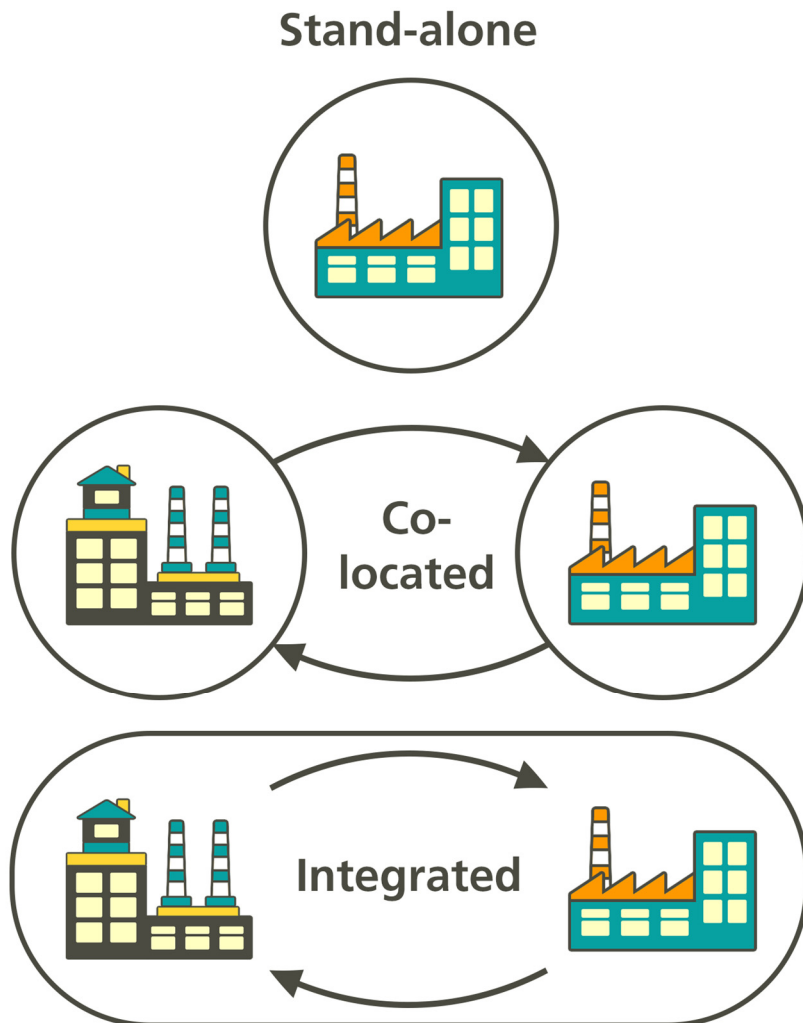


Figure 4.1 Illustration of the difference between stand-alone, co-located and integrated gasification plants. The black frames represent system boundaries.

the investment and operating cost of the biomass gasification and SNG production plants while simultaneously exploiting synergistic effects by exchanging material and energy streams with the host plant. Considerable advantages in biomass handling, logistics and heat integration could be obtained by integrating gasifiers into the forest industry, for example, at sawmills or pulp and paper mills.

According to a study by Wetterlund et al., a large number of industrial plants in Sweden are potentially suitable for biomass gasifier integration [31]. Figure 4.2 shows the geographical distribution of a selection of industrial plants that could be of interest in Sweden. They consist of district heating plants, pulp and paper mills, chemical plants, sawmills and steel mills. To further explore the viability of this production option, a review of industrially integrated biomass gasifiers for biofuel and biochemical production was performed in collaboration with Chalmers University of Technology, Linköping University and Luleå University of Technology. The detailed results of this review can be found in **Paper II**. The remainder of this chapter will be devoted to explaining the concept of industrial integration and discussing whether this is a viable option for SNG production.



Figure 4.2 Locations of industrial plants of interest for biomass gasifier integration in Sweden. Adapted from [31].

## 4.1 Industrially integrated gasification

In contrast to stand-alone gasification plants, integrated biomass gasifiers form an integral part of the host plant. This means that the two processes exchange resources, such as material streams and energy, to better utilize available process streams. Three different options for process integration are given by Nohlgren et al. [32]:

- Feedstock integration: to utilize existing internal material streams for conversion processes, for example, bark, black liquor, wood residues, etc.
- Energy integration: to utilize energy flows, for example, for fuel drying, pre-heating, heating systems, etc.
- Equipment integration: to utilize existing or new scaled-up equipment, such as air separation units, distillation columns, crackers, etc.

The definition of an integrated plant differs between publications. In **Paper II** the criterion for a gasification process to be considered industrially integrated is that a two-way exchange of material streams and/or energy takes place between the processes. According to this criterion, a gasification plant receiving feedstock from another plant without returning any form of material or energy to be utilized in the host plant, is not considered to be integrated, but instead seen as a co-located gasification plant.

### 4.1.1 Potential industrial plants

As can be seen in Figure 4.2, many Swedish industrial plants have the potential to act as host plants for integrated biomass gasifiers. Industrial plants where biomass is used in the process, such as pulp and paper mills or sawmills, are of great interest for gasifier integration as the feedstock is already on site. This is reflected in the results presented in **Paper II**, where the most commonly occurring type of host plant was chemical pulp and paper mills. Mechanical pulp and paper mills, sawmills, bioethanol plants and biodiesel plants are also represented in the reviewed material. The way in which a biomass gasifier is integrated into the host plant depends mainly on the type of host plant and its operating conditions.

In the case of chemical pulp and paper mills, a biomass gasifier can be integrated in two main ways. The first is to replace the traditional cooking chemical recovery process with black liquor gasification. In the traditional cooking chemical recovery process, concentrated black liquor is combusted in a recovery boiler in order to separate the inorganic cooking chemicals used in the pulping process from organic residues (fragments of lignin and hemicellulose). The heat from the combustion of the black liquor is used to produce steam and electricity for internal use in the mill. By replacing the recovery boiler with an entrained flow gasifier, it would be possible to utilize the black liquor for SNG production, while using the excess heat from the gasifier to generate steam and electricity. The second integration option is to integrate a fluidized-

bed gasifier to gasify excess bark, which would traditionally be combusted in a bark boiler for steam generation. According to Pettersson et al., a drawback of both options is that the integration of a biomass gasifier would require a substantial increase in biomass input in order to maintain the original output capacity of the host plant [33].

Industrial plants not traditionally associated with biomass processing, such as steelworks or oil refineries, were also found in the reviewed material. None of these publications had SNG as the target chemical, and will therefore not be discussed further in this chapter. However, this does not mean that the integration of SNG production in these types of plants is not possible.

## 4.2 System performance

It is often not possible to make accurate and reliable comparisons of the performance of different systems in different integration concepts found in the literature due to variations, for example, in system boundaries or system efficiency calculation methods. However, it is possible to obtain an indication of the added value and extra cost the in process, and thus to indirectly evaluate different integration concepts, by studying the incremental change in operation, i.e., the additional supply of biomass and energy carriers required to produce SNG, compared to the stand-alone operation of the host plant. This was done by calculating and comparing system efficiencies for different concepts. System efficiencies ( $\eta$ ) were calculated as the fraction of all energy (Q) inputs and outputs expressed in MW, Eq. 4.1.

$$\eta = \frac{\sum Q_{output}}{\sum Q_{input}} \quad (4.1)$$

When using incremental mass balances, different approaches can be used to account for changes in the original operation. One common situation is when the plant exports electricity both prior to and after integration, however, the export is lower in the integrated case. This change can be accounted for either as a reduction in export (negative output), or as an increase in power demand (positive input). As system efficiency calculations are based on fractions, using different approaches in the calculations will cause discrepancies. To avoid negative values in the system efficiency calculations reductions in export were accounted for as an input, and vice versa.

System efficiencies were calculated according to Eq. 4.1 for 18 different integrated biomass gasification concepts, and the results are shown in Figure 4.3. The cases were taken from eight different publications on integrated biomass gasification, in which



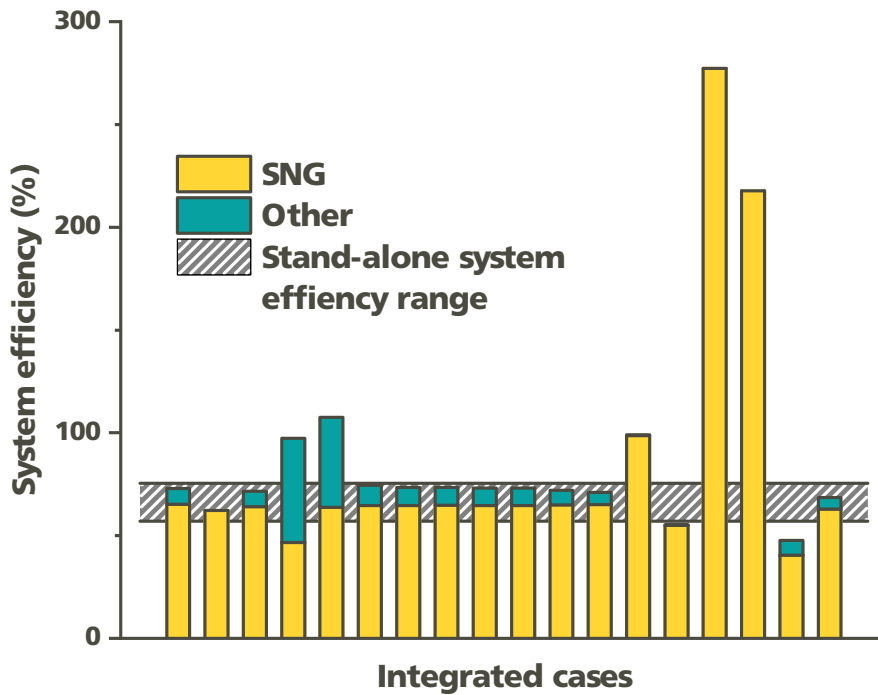


Figure 4.3 Calculated system efficiencies for 18 cases of integrated biomass gasification with SNG production from 8 publications. “Other” includes electricity, Fischer-Tropsch fuels, steam and district heating. The grey hatched area shows the range in system efficiency of two SNG-producing stand-alone gasification plants found in the literature.

various types of gasifiers were integrated in different industrial plants [34–41]. Figure 4.3 also shows the range in system efficiency of two SNG-producing stand-alone gasification plants from the literature [42,43]. This range provides an indication of the performance of the integrated cases compared to more traditional production methods.

As can be seen in Figure 4.3, the majority of the cases exhibit a system efficiency just above 70%, which lies well within the reference range for stand-alone plants, indicating that industrially integrated SNG production has the same performance as stand-alone production. A few cases show system efficiencies exceeding 100%, which is not uncommon when incremental values are used for system efficiency calculations. This anomaly can occur when previous internally available feedstock or energy surplus is used in the integrated case at the expense of export revenue, for example, bark being gasified for SNG production instead of being exported.

### 4.3 Economic performance

In order to compare the cost of integrated SNG production with that of stand-alone production, the integrated production facility was regarded as a separate entity and not as part of the host industry. All the additional costs for the host plant associated with the integration of SNG production will thus have to be covered by the revenue generated by SNG sales, and the production cost of the SNG together with the investment cost required for integration are therefore of great importance. Of the eight publications considering SNG production that were studied, only two contained economic calculations for a total of eight cases.

Comparing investment and operational costs between different publications is often not meaningful due to a significant spread in the year of publication, and the lack of accounting for inflation and monetary exchange rates. For such comparisons to be meaningful, the investment costs were updated to values in 2016 using the Chemical Engineering Plant Cost Index [44]. Figure 4.4 shows the specific investment cost (incremental investment cost per MW SNG produced) for the eight cases found in the reviewed material. Six stand-alone cases from Gassner & Maréchal [43] are included for comparison.

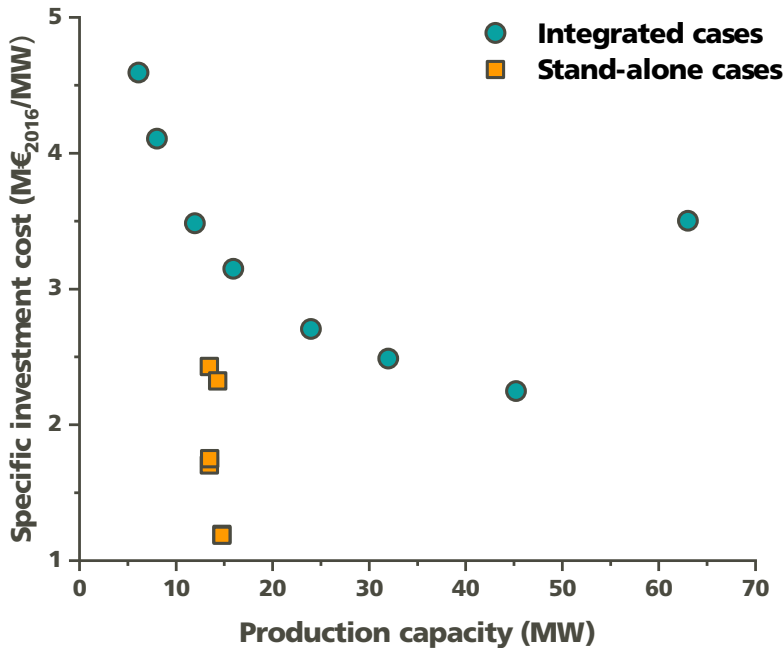


Figure 4.4 Calculated specific investment costs for integrated and stand-alone cases of SNG production as a function of production capacity.

The specific investment cost for the integrated cases ranges from 2.2 to 4.6 M€ per MW SNG produced. It is, however, important to note that seven out of the eight cases stem from the same publication, and the calculations were therefore based on the same process unit scaling factors. The specific investment costs are lower for the stand-alone cases; however, as all cases had approximately the same production capacity, it is not possible to determine whether there would have been an economy-of-scale effect.

The operational cost is more difficult to streamline as the variation between utility costs in the publications is greater than inflation in the price. Using indexation methods for price streamlining is therefore not considered any more accurate than other estimation methods. A rough estimate was made by calculating the average cost for each utility using the values presented in all publications, including publications not dealing with SNG production. This will give more reliable averages as the dataset is larger. These average values were used in combination with the investment cost to calculate final production costs, which are given in Table 4.1. Production costs were also calculated for six stand-alone cases from Gassner & Maréchal [43] using the same economic input values as for the integrated cases.

**Table 4.1 Average utility costs and calculated SNG production costs (€/MWh)**

	Average	Max	Min	Standard deviation
Biomass	15.5	28.0	4.9	6.3
Electricity	50.4	68.0	25.0	15.1
Depreciation (years)	20.7	25	10	4.6
Weighted average cost of capital	8.7%	13.1%	4.1%	1.4%
Integrated SNG production cost	86	113	69	16
Stand-alone SNG production cost	54	66	41	10.5

The Swedish price of natural gas for household consumers during the second half of 2017 was 110 €/MWh (including taxes), and 47 €/MWh for commercial customers, according to Eurostat [45]. According to the results listed in Table 4.1, it would be possible to produce SNG at a cost low enough for SNG to be competitive with household prices. Current commercial prices, on the other hand, are still significantly lower. As the combined heat and power and industrial sectors accounted for about 80% of the Swedish natural gas consumption in 2016 [46], the production cost of SNG must be further reduced if integrated production is to be considered profitable. Stand-alone production costs are significantly lower; the lowest calculated production cost of 41 €/MWh being on a par with that of commercial gas prices. However, these costs are highly uncertain due to the assumptions made in the calculations.

## 4.4 The Swedish context

Although the concept of producing SNG via biomass gasification in Sweden might seem promising in theory, due to high system efficiencies, this is not the case in reality. SNG still struggles to be economically competitive with natural gas, a fact that manifested itself earlier this year, when it was decided that all current operations at GoBiGas, Sweden's only SNG production plant, were to be discontinued until further notice due to the plants economic difficulties. Furthermore, although the concept of industrially integrated gasification has been researched for more than a decade, little or no interest has been shown by industry in adapting any of the concepts evaluated. Reasons for this reluctance might be the current lack of proof-of-concept facilities, or unwillingness to spend substantial capital without long-term government incentive structures, despite the possible benefits that integration might bring. Based on the results presented in this chapter their reluctance may be well grounded as, although SNG system efficiencies in integrated production do not differ significantly from those in stand-alone production, the production costs in the cases studied are too high to be competitive on the open market, which is imperative for any business concept. Biomass costs account for a large part of the production cost due to the high amount needed in the gasification process. Switching to a cheaper feedstock would thus lead to reduced costs. However, as the quality of the feedstock often decreases with the price, it is necessary to develop gasification processes that are more robust and efficient if the same output is to be achieved as when high-quality fuels are used. It therefore appears that there will be no further developments of any form of SNG production using biomass gasification in the foreseeable future.



# 5

## Plant improvements

The final topic covered in this thesis is the possibility of process improvements in biomass gasification and SNG production. As in many industrial plants, a number of factors could perhaps be improved or optimized in order to achieve higher yields and better economy. A common area of research and development in biomass gasification processes is gasifier design, and research is being carried out on different types of gasifiers of various scales at several Swedish universities, such as the Luleå University of Technology, the Royal Institute of Technology in Stockholm and Chalmers University of Technology in Gothenburg. The aim of this research is, amongst other things, to improve biomass conversion and gas component yields, and reduce tar formation.

Another important area of research is in producer gas cleaning. Various impurities must either be removed from the gas or be converted into other substances before it can be treated in subsequent process steps. Impurities often lead to problems in downstream processes, such as damage to equipment in SNG synthesis. In addition, the concentrations of some impurities in the SNG must be below certain limits before the gas can be injected into a gas grid. Table 5.1 gives the limits specified for the Swedish gas grid [47,48].

The most significant impurities generated during biomass gasification are tars. Tars may condense, causing fouling and clogging, or damage to downstream equipment. Considerable effort is therefore made in the gasification industry to remove tars, either mechanically, using filters or scrubbers, or by reforming them into smaller compounds, using thermal or catalytic cracking [49]. Cracking the tars allows their energy and mass to be retained in the producer gas, thus providing higher amounts of gas in the SNG

**Table 5.1 Limits on levels of impurities in SNG in the Swedish gas grid**

Compound	Limit
CH <sub>4</sub> (mol%)	≥ 65
CO <sub>2</sub> (mol%)	≤ 2.5*
H <sub>2</sub> (mol%)	≤ 2
Total sulphur (mg/Nm <sup>3</sup> )	≤ 20
Ammonia(mg/Nm <sup>3</sup> )	≤ 3
Siloxanes (mg/Nm <sup>3</sup> )	≤ 0.4
Hydrocarbon dew point (°C at 7 bar (a))	≤ -2

\*The limit ≤ 2.5 applies to the Swedish transmission gas grid. CO<sub>2</sub> contents up to 4 mol% can be allowed in local distribution grids.

production process. **Paper III** presents a proof of concept for a novel regenerative reverse-flow reactor containing calcinated dolomite, which is catalytically active for tar-cracking reactions. A disadvantage of using cracking for tar removal is the increase in both investment and operational costs, as the cracking process requires additional reactors, catalysts and large amounts of energy in order to break up the molecular structure of the tars [50]. The balance between the additional costs and improved producer gas yield will probably be beneficial in larger gasification plants due to economy-of-scale effects. Smaller plants on the other hand will not benefit from the investment due to the additional operational costs. Using a scrubber to remove the tars from the producer gas is a technically much simpler process than cracking, and would therefore be more suitable in smaller gasification plants. However, in order for scrubbing to be economically viable, it is necessary to recover and reuse the scrubber liquid, as the cost of the scrubber liquid and its disposal after use represents a considerable part of the operating cost. **Paper IV** describes how this cost could be decreased by regenerating the scrubber liquid using centrifugation.

Another impurity formed during gasification is ammonia. Ammonia can cause poisoning of some catalysts [51–53], however, the major concern regarding ammonia is that it forms nitrous oxides (NO<sub>x</sub>) when combusted. This is of great significance as most of the renewable gas currently produced in Sweden is used as vehicle fuel in the transport sector. The level of ammonia in producer gas obtained from the gasification of woody biomass generally varies from 0.1 to 1.5 mg/Nm<sup>3</sup>, but can be over 8 mg/Nm<sup>3</sup> when using other biomass feedstocks [53]. These levels are significantly higher than the current limit of 3 mg/Nm<sup>3</sup> (Table 5.1). In **Paper V**, the possibility of converting ammonia into nitrogen and water using selective catalytic abatement with NO<sub>x</sub> is discussed.

The remainder of this chapter will focus on concepts for the removal of tar and ammonia from producer gas obtained by biomass gasification. Section 5.1 is based on the studies presented in **Papers III** and **IV**, while Section 5.2 is based on the work described in **Paper V**.

## 5.1 Tar removal

Various technologies are available for the removal of tars from producer gas, each with advantages and disadvantages depending on the scale of the gasification plant. Two different tar removal processes were examined in the present work. The first was thermal cracking, which has the advantage of decomposing the tars into smaller compounds that can be utilized in the process. However, it is a rather advanced technology, and is only economically viable in large-scale plants. The other process investigated is scrubbing, which physically removes the tars, and is more suitable in smaller gasification plants. The possibility of regenerating the scrubber liquid to reduce the operational costs of tar scrubber systems was therefore investigated.

### 5.1.1 Thermal cracking

As tars consist mainly of polyaromatic hydrocarbons it is beneficial to decompose them into smaller hydrocarbons, so as to retain the energy and mass of the tars and utilize the new compounds together with the producer gas. Removing the tars entirely, instead of converting them, thus leads to a loss of valuable material. The catalytic cracking of tars has been well researched, and many publications can be found on the subject [54–56]. Examples of catalysts that have been shown to perform well in tar-cracking applications are Ni-based catalysts, dolomite and olivine. Ni-based catalysts are available at relatively low cost, but they are highly sensitive and easily deactivated by sulphur compounds, which are inevitably present in producer gas. Calcined dolomite is resistant to sulphur poisoning, and is already being used in biomass gasification applications, both as a catalytically active bed material in fluidized-beds and in gas-cleaning processes [57–60].

In the present work (**Paper III**), calcined dolomite was used as a catalyst in a regenerative reverse-flow reactor for tar cracking. These reactors have a relatively simple design, and consist of a stationary catalytic bed enclosed in a vessel with inlets at each end. When the reaction gas passes through the stationary reactor bed, heat is transferred from the exiting gas to the bed, creating a thermal buffer. When the flow is reversed, the heat stored in the buffer is transferred to the gas entering the reactor. Thus, the catalytic bed consists of two alternating thermal buffer zones with an active reaction zone in between. A detailed description of the reverse-flow reactor system has been published by Matros and Bunimovich [61]. Figure 5.1 illustrates the different reactor zones and the temperature profile throughout the reactor.

Reverse-flow reactors are traditionally used in exothermic applications, such as the catalytic oxidation of volatile organic compounds and partial oxidation of methane for producer gas production, but Van de Beld et al. demonstrated that the technology is also suitable for tar cracking [62]. The reactor they used contained bauxite in the thermal buffer zones and calcined dolomite in the active zone, and was operated at temperatures around 1050 °C. This configuration led to high energy losses and a high



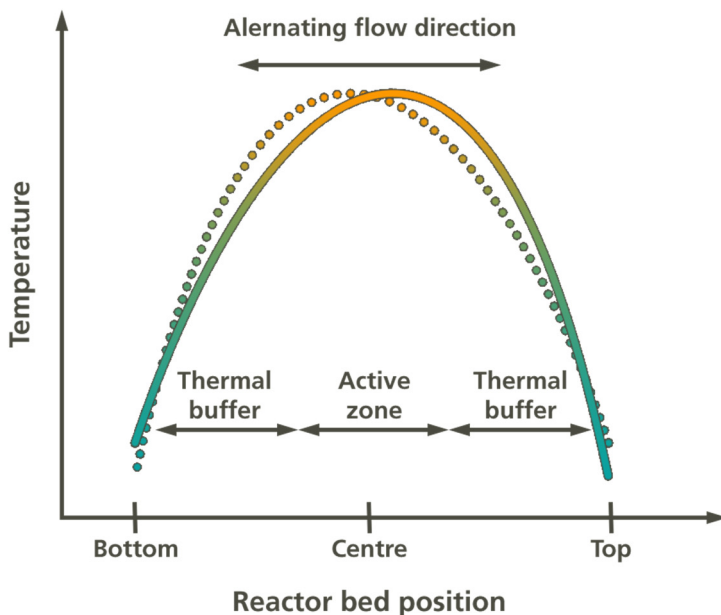


Figure 5.1 Schematic illustration of the reactor zones and the temperature profile in a reverse-flow reactor.

risk of soot formation on the catalyst, which reduce the catalytic activity. In response, Svensson et al. developed a model to predict soot formation during partial oxidation of producer gas based on different producer gas compositions [63]. The results showed that soot formation was largely dependent on the methane and tar contents of the producer gas.

In order to improve the concept of the regenerative reverse-flow reactor for tar cracking, a bench-scale set-up was constructed, using calcined dolomite, and operated under 1000 °C in order to avoid soot formation. The aim was to crack a large tar compound and convert it into producer gas compounds. A model producer gas was prepared using 1-methylnaphthalene (1-MN) as a model compound for tertiary tars, with the composition given in Table 5.2. The reactor was operated at active zone temperatures

**Table 5.2 Gas composition (vol%) of the model producer gas**

Component	Volumetric fraction
CO	25
CO <sub>2</sub>	15
H <sub>2</sub>	25
CH <sub>4</sub>	10
H <sub>2</sub> O	25
1-MN (mg/Nm <sup>3</sup> )	15 000

of 700, 800 and 850 °C, and at gas flow rates of 0.5, 0.85 and 1.2 Nm<sup>3</sup>/h, which correspond to gas hourly space velocities of 45, 75 and 105 h<sup>-1</sup>, and residence times of 29, 17 and 12 seconds, respectively. Both fresh and used catalyst was characterized, and the details can be found in **Paper III**.

The conversion efficiency of 1-MN can be expressed in different ways. The conversion efficiency was expressed in two different ways to better reflect the overall tar-cracking performance of the reverse-flow reactor. The first considers the conversion of 1-MN into any other compound with a lower mass, and is expressed as  $(1-MN_{in} - 1-MN_{out})/1-MN_{in}$ . The second method considers further conversion of the light tar compounds (e.g., benzene, toluene, xylene and naphthalene) formed during the decomposition of 1-MN, and is expressed as  $(1-MN_{in} - Tar_{out})/1-MN_{in}$ . The results are shown in Figure 5.2.

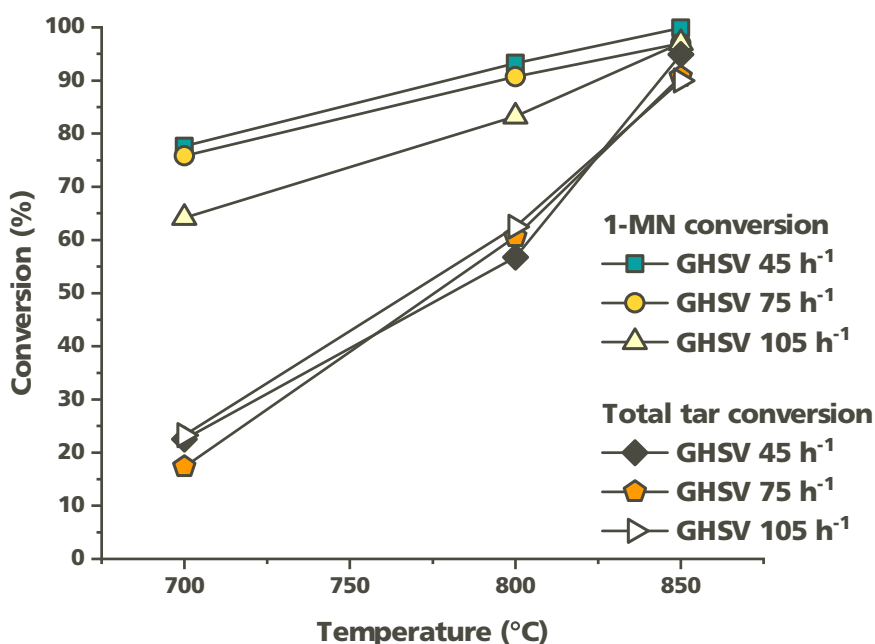


Figure 5.2 Tar conversion efficiency in the bench-scale regenerative reverse-flow reactor, using the two methods described above. (GHSV= gas hourly space velocity).

The system showed good conversion of 1-MN over the entire temperature range, reaching a maximum of 99%. However, at lower temperatures, 1-MN was mainly converted into light tars, as reflected by the low total tar conversion obtained at all gas space hourly velocities. A large proportion of the tars leaving the reactor at 700 °C consisted of naphthalene, indicating that the initial step in the cracking of 1-MN is the removal of the methyl group from the aromatic rings. Increasing the reaction temperature in the active zone allowed the stable ring structures to be broken, thus

increasing the total tar conversion from about 20% to 95%. It is thus recommended that the reactor be operated at temperatures above 800 °C.

Regenerative reverse-flow reactor technology has the potential to become a highly efficient process in the biomass gasification gas cleaning train. However, experiments must first be carried out using producer gas generated in an actual gasifier, as real producer gas contains other compounds that might affect the operation of the reverse-flow reactor.

### 5.1.2 Scrubber liquid regeneration

Scrubbing is a widely used gas-cleaning technology and is often used for tar removal in biomass gasification plants [64,65]. Although many studies have been carried out on the absorption of volatile organic compounds and tars by various scrubber liquids [66–69], little information could be found in the literature on the possibility regenerating the scrubber liquid after use. Commercial tar-scrubber systems including scrubber liquid regeneration are available; the most well-known being the OLGA process developed by the Energy Research Centre of the Netherlands [64]. However, the complexity of these systems makes them unsuitable for use in some small-scale applications. A cheap and simple method of separating tar from a scrubber liquid is centrifugation; centrifuges have long been used in the coal tar and coke industry to separate different tar fractions [70,71]. Tarnpradab et al. showed that it was possible to efficiently regenerate tar-saturated canola oil using centrifugation, with the regenerated oil exhibiting an absorption efficiency close to that of fresh oil [72].

Diesel and rapeseed methyl ester (RME) are commonly used as scrubber liquids in applications involving hydrophobic compounds, and were chosen together with five other potential scrubber liquids found in the literature (linoleic acid, linseed oil, motor oil, rapeseed oil and silicone oil) for the regeneration experiments described in **Paper IV**. Only the results for diesel and RME will be discussed here as these vastly outperformed the other five liquids studied. Spent scrubber liquid obtained from a Swedish biomass gasification plant was used to create model spent scrubber liquids for use in the experiments. The diesel or RME was mixed with water, wood tar and a tar/ash mixture (sludge), also obtained from the biomass gasification plant. The composition is given in Table 5.3. The model spent scrubber liquids were transferred

**Tabell 5.3 Model spent scrubber liquid composition**

<b>Component</b>	<b>Amount (wt%)</b>
Scrubber liquid	50
Water	5
Wood tar	5
Sludge	40

to 15 ml glass tubes and the samples were heated to 50, 70 or 90 °C before being run in a Thermo IEC Centra CL2 benchtop centrifuge for 1.5, 5 or 10 minutes.

During centrifugation, the samples separated into a highly viscous bottom phase, containing sludge, water and small amounts of scrubber liquid and heavy wood tars, and a low-viscosity top phase, containing the scrubber liquid (diesel or RME) and light wood tars. Samples that had been heated at lower temperature and centrifuged for short times also contained an intermediate phase, indicating that separation is better at higher temperatures and longer centrifugation times (Figure 5.3). The recovery of the scrubber liquid was calculated as  $(m_{\text{top phase}} + m_{\text{intermediate phase}})/m_{\text{scrubber liquid}}$ , where  $m$  donates mass, and the results obtained are presented in Table 5.4.

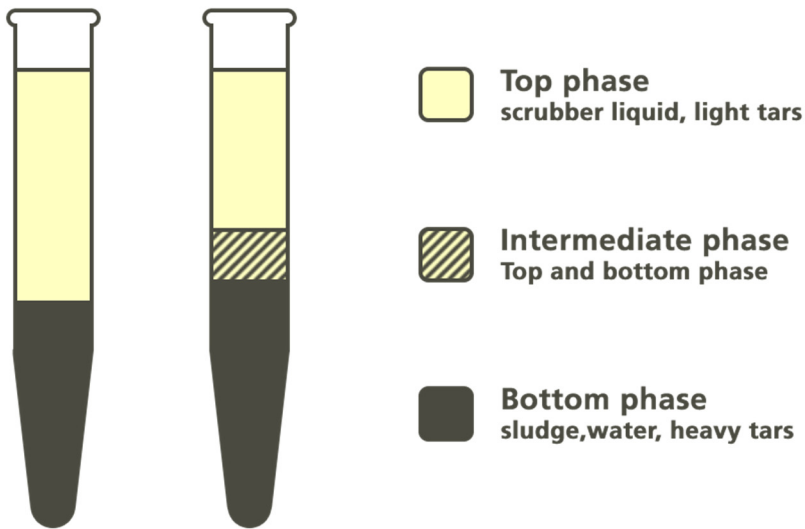


Figure 5.3 Appearance of model spent scrubber liquid samples after centrifugation: left: at higher temperatures for longer times and right: at lower temperatures for shorter times.

**Tabell 5.4 Recovery of scrubber liquid (%) after centrifugation at three temperatures and for different times (Italics indicate samples containing an intermediate phase.)**

Temp./time	Diesel			RME		
	1.5 min	5 min	10 min	1.5 min	5 min	10 min
50 °C	81	105	111	<i>132</i>	<i>109</i>	101
70 °C	89	108	112	<i>122</i>	94	103
90 °C	94	109	111	96	93	104

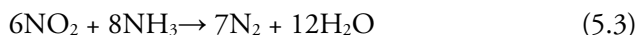
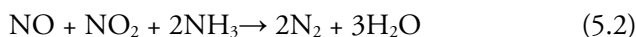
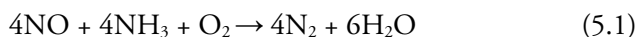
All except one of the diesel samples separated into two distinct phases, regardless of the temperature or separation time, while the RME samples required higher temperatures and longer separation times in order to achieve the same degree of separation as the

diesel samples. Due to the low viscous nature of the intermediate phase it was not possible to separate it completely from the top phase, which resulted in recovery values exceeding 100% in some cases. Some of the samples without the intermediate phase also gave values exceeding 100% due to light tars having dissolved in the scrubber liquid. Thus, only heavy, insoluble tar compounds can be separated from the scrubber liquid using centrifugation, while light, soluble compounds will accumulate over time. It is difficult to predict how this could affect the scrubber efficiency without performing long-term experiments. It might suffice to bleed off a fraction of the used scrubber liquid and replace it with fresh scrubber liquid, however, no information on this could be found in the literature.

Although diesel performed better than RME as a scrubber liquid, the use of a fossil-based scrubber liquid in a process developed to produce renewable gas is questionable. Thus, RME is recommended as a scrubber liquid in biomass gasification plants.

## 5.2 Ammonia removal

Several technologies are available for the removal of ammonia, however, few are suitable for use in biomass gasification plants. Scrubbing the producer gas with water would be the simplest option as the solubility of ammonia in water is high. However, due to the presence of tars in the gas this option should be avoided as the separation of water/tar/ash mixtures is difficult. An RME scrubber could be used instead for the simultaneous removal of tars and ammonia [73]. In biomass gasification plants without scrubbers, other methods of ammonia removal could be applied. Ammonia can be removed by selective catalytic oxidation with air or oxygen [20]. However, due to the low levels of oxygen in producer gas this method is of little relevance in this application. Selective catalytic reduction (SCR) is a well-known industrial process used for the removal of NO<sub>x</sub> from combustion flue gases, using ammonia or urea, and the conversion proceeds according to reaction 5.1-5.3 [74,75]. Tunå & Brandin have demonstrated that the reverse reaction, selective catalytic oxidation of ammonia, is possible under a reducing atmosphere and in the presence of a suitable catalyst.



**Paper V** describes the use of selective catalytic oxidation for the removal of ammonia from a model producer gas under both dry and wet conditions, as water is known to lower the activity of SCR catalysts. The gas compositions are given in Table 5.5. Two different catalysts, both known to promote the SCR reaction were chosen: V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> and H-mordenite (zeolite). These catalysts differ in their

composition, structure and operation temperature; H-mordenite being active and selective in a higher temperature range (290-450 °C) than the vanadium-based catalyst (300-400 °C). A detailed description of the experimental set-up can be found in Paper V.

**Tabell 5.5 Gas compositions used in the dry and wet selective catalytic oxidation experiments**

Compound	Dry		Wet	
	ml/min	vol%	ml/min	vol%
NH <sub>3</sub>	0.75	0.28	0.75	0.25
NO <sub>2</sub>	0.75	0.28	33.75	11.25
CO	33.75	12.68	33.75	11.25
CO <sub>2</sub>	33.75	12.68	33.75	11.25
H <sub>2</sub>	33.75	12.68	33.75	11.25
N <sub>2</sub>	163.5	61.40	163.5	54.5
Total	266.25	100	300	100

In order for a catalyst to be deemed suitable for ammonia abatement it must be able to convert ammonia into other compounds. However, the compounds into which the ammonia is converted are also important, as conversion into NO<sub>x</sub> would defeat the purpose of the entire concept. Figure 5.4 shows the ammonia conversion achieved and the selectivity towards nitrogen (N<sub>2</sub>), nitric oxide (NO) and nitrous oxide (N<sub>2</sub>O), for both dry and wet conditions.

Based on these initial results, the vanadium-based catalyst is appeared to be better suited than the mordenite catalyst under the conditions investigated. It can be seen from Figure 5.4a that the conversion of ammonia was consistently higher using the vanadium-based catalyst, with conversion efficiencies of 99% and 97% under dry and wet conditions, respectively. The concentration of ammonia would thus be well below the limit for the Swedish gas grid of 3 mg/Nm<sup>3</sup>. The presence of water in the reaction gas causes the activity of the mordenite catalyst to fall drastically, while the vanadium catalyst remains virtually unaffected. An interesting observation is the increased selectivity of the vanadium catalyst towards N<sub>2</sub> under wet conditions (Figure 5.4b). As can be seen in Figure 5.4c, the NO selectivity is low for both catalysts. The most significant difference between the catalysts is seen in their selectivity towards N<sub>2</sub>O (Figure 5.4d), which is much lower for the vanadium-based catalyst. Although these experiments showed very promising results for the vanadium-based catalyst, the activity of the catalyst decreased by about 10% during long-term experiments lasting 100 hours, indicating that the catalyst is not chemically stable in the reducing environment. This is due to the active V<sub>2</sub>O<sub>5</sub> phase being reduced to other oxides and elemental vanadium. The H-mordenite outperforms the vanadium catalyst in long-term experiments as the zeolite structure of H-mordenite is highly stable.

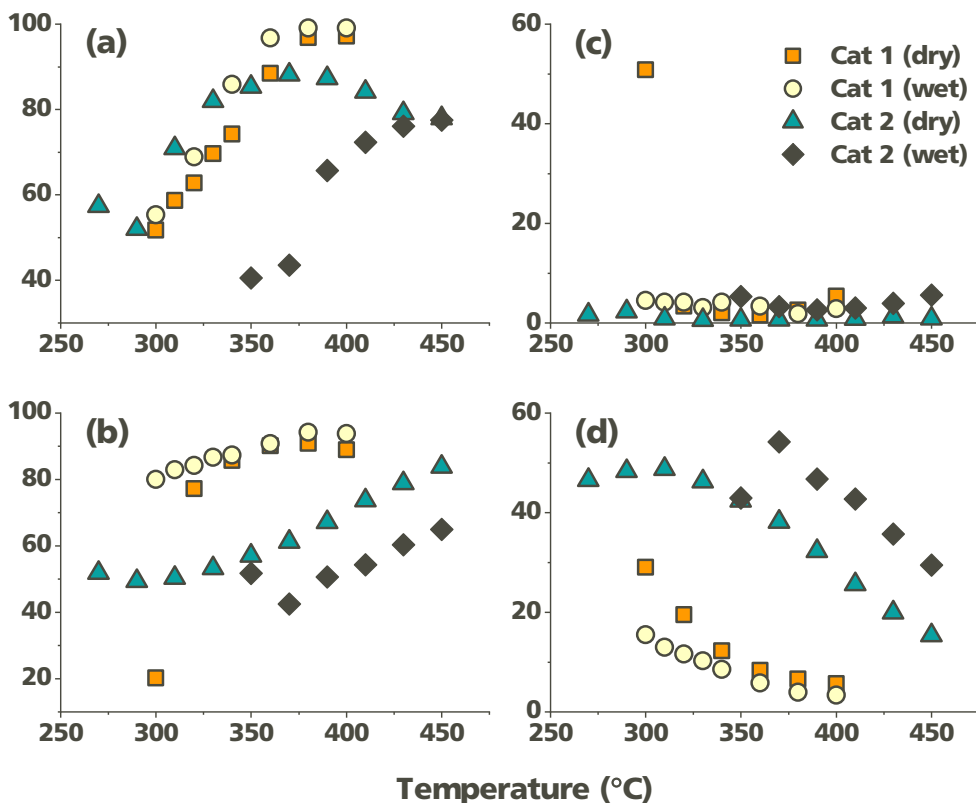


Figure 5.4 Ammonia conversion (a),  $N_2$  selectivity (b),  $NO$  selectivity (c) and  $N_2O$  selectivity (d) performance of  $V_2O_5/WO_3/TiO_2$  (Cat 1) and H-mordenite (Cat 2).

Neither of these catalysts is recommended for industrial implementation in their current state. The vanadium catalyst is not stable in the reducing atmosphere, and another active phase should be used instead. The selectivity of the H-mordenite could be improved by replacing the active hydrogen in the zeolite structure with another ion, i.e. Ce. Another option is to search for a more suitable zeolite. If these catalysts could be improved they may have considerable potential as commercial catalysts for ammonia abatement using selective catalytic oxidation.

### 5.3 The Swedish context

As with natural gas, renewable SNG must meet certain quality criteria in order to be approved for injection into the grid. It is thus imperative that SNG free from impurities can be produced if Swedish SNG production is to expand. The aspects of gas cleaning

discussed in this chapter are therefore highly important in improving Swedish biomass gasification for SNG production. As each plant is unique in terms of its feedstock and operating conditions, different problems will have to be solved from case to case. This chapter describes how various innovative methods for the removal of tars and ammonia were investigated in order to identify gas-cleaning techniques that have potential for development for industrial use. Research is being performed in both gas scrubbing and catalytic tar removal. Several papers have recently been published on the tar-cleaning performance of various scrubber liquids [72,76,77], as well as on catalytic tar reforming [78–80].

Producer gas contains several other impurities that must be considered in biomass gasification. One area of special interest is sulphur poisoning and the development of sulphur-resistant catalysts [81–83]. As mentioned previously in this chapter, and as was shown in Chapter 2, gas cleaning is only one stage in the production of SNG. Research and development are being carried out throughout the production chain, to study different biomass pre-treatment options [84,85], gasifier designs [86,87] and SNG synthesis processes [88,89]. The future development of more effective catalysts and the processes of gasification and SNG synthesis will hopefully enable a wider range of feedstocks of varying quality to be used in biomass gasification.







## Concluding remarks

The work described in this thesis was directed at answering the question: “What measures are, and needs to be, taken to facilitate the implementation and expansion of SNG production and use in Sweden?”. Research has been performed on three different levels in order to identify innovative solutions to the challenges present throughout the entire SNG production chain, from biomass gasification to SNG distribution. Four specific research questions were addressed.

### *How can the distribution of SNG be improved?*

The issue of SNG transportation and distribution was examined, and it was found that Swedish SNG would benefit from being distributed via the Swedish gas grid. However, injecting renewable gas into the grid will cause local fluctuations in gas quality due to mixing of gases of different quality. In a joint project with E.ON, strategies were developed for the determination of heating values in gas grids with multiple injection points, and the project culminated in the Swedish gas industry standard being updated to include these types of grids, the use of quality trackers, as well as requirements on the accuracy and control of heating values determined with quality tracking. Several gas grid actors have implemented quality tracking, allowing them to predict and monitor heating values with great accuracy, regardless of the level of grid complexity. This is of great advantage as it enables expansion of the Swedish gas grid, thus facilitating the future inclusion of both SNG and biogas production plants. The most significant implication, however, is that quality tracking will eliminate the need for propanation in the long term, and thus the current practice of adding fossil propane to renewable gas will cease.

### *Can SNG compete with natural gas?*

The possibility of producing SNG as an integrated part of another industrial plant was investigated. Although integrated SNG production systems can exhibit system efficiencies similar to those for stand-alone production plants, the cost of production is currently too high for SNG to be competitive with natural gas. According to the results, the lowest calculated production cost is 69 €/MWh, which is well above the price of natural gas for commercial customers, of 47 €/MWh. Improvements must be made in both biomass gasification and SNG production if production costs are to be lowered. As the cost of biomass is one of the factors contributing most to the overall cost of SNG production, the availability of low-cost biomass could contribute to reducing the production cost. However, as discussed in Chapter 2, switching to low-cost feedstock may well mean a reduction in feedstock quality, placing higher strain on the production process. There is a clear need for incentives and subsidies if SNG is to be competitive at the current production cost.

### *What are the challenges in individual production plants?*

Efficient gas cleaning is one of the most crucial aspects of biomass gasification, and the techniques used are under constant development. Thus, novel approaches for the removal of tar and ammonia from producer gas were investigated.

A regenerative reverse-flow reactor was constructed as a proof of concept for the cracking of tars using calcinated dolomite as bed material. The results showed good conversion rates, up to 99%, of 1-MN into smaller compounds, while total tar conversion reached 95% when operating the reactor above 800 °C. These results indicate that regenerative reverse-flow reactor technology has the potential to become a highly efficient process step in a biomass gasification gas-cleaning train. For biomass gasification plants using scrubbers for tar removal, scrubber liquid regeneration using centrifugation was proposed as a way of reducing the operational cost. Centrifugation was proven to efficiently regenerate tar-contaminated RME and diesel, and the results indicated that separation is favoured by higher temperatures and longer centrifugation times. Although separation was slightly better using diesel as a scrubber liquid, RME is considered to be more suitable for use in a renewable SNG plant than diesel from fossil sources.

Ammonia removal experiments were performed by applying the reverse SCR reaction in a reducing atmosphere. The ability of two well-known SCR catalysts,  $V_2O_5/WO_3/TiO_2$  and H-mordenite, to convert ammonia into nitrogen gas was evaluated. The vanadium-based catalyst showed promising initial performance regarding ammonia conversion and nitrogen selectivity, but proved not to be chemically stable during long-term experiments, where a 10% reduction in activity was seen. H-mordenite exhibited no changes in activity during long-term experiments, but performed less well than the vanadium-based catalyst in every other respect. Neither of

the catalysts performed satisfactorily in their current state, and would have to be improved if they are to be implemented in industry.

### *Is there a future for SNG in Sweden?*

Based on the results presented in this thesis, the current outlook for Swedish SNG production by biomass gasification is not very promising. Although there are well-functioning systems in place for SNG distribution, the production of SNG is currently not sufficiently efficient for SNG to be produced at a cost that is competitive with that of natural gas. The main use of natural gas in Sweden is currently as a fuel for industrial heat and power production. Producing renewable SNG from biomass can thus be regarded as a wasteful detour compared to using the biomass directly for combined heat and power production. Transforming biomass into a useful vehicle fuel is a far better use of renewable resources, however, without clear regulations regarding the end use of renewable SNG, it would be more beneficial to produce liquid fuels, such as Fischer-Tropsch fuels or dimethyl ether via biomass gasification, than SNG.

Regardless of the current situation in Sweden, renewable SNG concepts are still being developed internationally. In the United Kingdom, the companies Cadent, Advanced Plasma Power and Carbotech Gas Systems GmbH came together to demonstrate the feasibility of renewable SNG production from biomass and waste [90]. The concept was successfully demonstrated at a pilot plant, and has led to the construction of a commercial facility planned to start operation in 2018.

The constant inflow of new research and development of various aspects of biomass gasification processes shows that there is continued interest in the subject, from the research community, industry and governmental bodies alike. This development will most definitely contribute to the transition towards a world based on renewable resources.

## **6.1 Future work**

There is room for a great deal of progress to be made at all three levels of SNG production. On the distribution level, further developments towards a greener gas grid could be made by investigating the possibility of ceasing the practice of propanation of renewable gas. This would not only reduce the consumption of fossil propane in the renewable gas sector, but also make production cheaper. Guidelines should be developed on how techno-economic studies should be carried out on integrated biomass gasification systems. The current lack of consensus between different research groups makes comparisons of different integration concepts difficult. At the production plant level, it is necessary to perform the experiments described in Chapter 5 on real producer gas from a gasifier, in order to fully evaluate the performance of the various

technologies. Several compounds present in the producer gas, such as tars and sulphur compounds, might have a considerable negative impact on the performance of both the regenerative reverse-flow reactor and the catalysts. As the catalysts used for selective catalytic oxidation of ammonia did not provide satisfactory results, screening of other catalysts is necessary in order to identify catalysts more suited for use under reducing conditions. In the case of the regenerative reverse-flow reactor, the tar-cracking performance of other bed materials of different particle sizes should be examined. In addition, long-term experiments should be carried out to investigate possible deactivation of the bed material. Tar centrifugation experiments should be performed on a larger scale, preferably at a biomass gasification plant. This would provide an opportunity to study how the accumulation of light tars in the scrubber liquid affects the scrubber efficiency over time.

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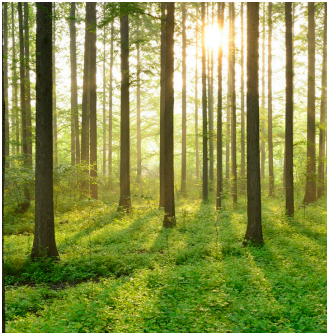
Paper I





# MEASURING AND ENSURING THE GAS QUALITY OF THE SWEDISH GAS GRID

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ENERGY GAS TECHNOLOGY







# Measuring and ensuring the gas quality of the Swedish gas grid

LAURA MALEK AND CHRISTIAN HULTEBERG

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Energiforsk AB | Phone: 08-677 25 30 | E-mail: [kontakt@energiforsk.se](mailto:kontakt@energiforsk.se) | [www.energiforsk.se](http://www.energiforsk.se)



## Authors' foreword

This project evaluated national standards from several European countries to address the issues with increasing variation of the gas quality in the Swedish gas grid arising from an increased content of gas from renewable sources.

The report has been produced by Lund University and the author is Laura Malek and Christian Hulteberg. Fredric Bauer is acknowledged for his invaluable help in finalizing the report.

The study was funded by the Swedish Energy Agency, through the Swedish Energy Research Centre and the Co-operation Program Energy gas technology, and E.ON Gas Sverige AB. The study had a reference/working group with the following members: Anna Gulin (E.On), Dan Lilja (E.On), Geir Sjöholm (Swedegas), Mattias Wesslau (Swedegas), Bernt Nyman (Kraftringen).

Reported here are the results and conclusions from a project in a research program run by Energiforsk. The author / authors are responsible for the content and publication which does not mean that Energiforsk has taken a position.

## Sammanfattning

**När mer förnybar gas produceras och exporteras till naturgasnätet uppstår en ny situation för nätoperatörerna, men i förlängningen även för kunderna, vad gäller mätning och säkerställning av gaskvaliteten på gasnätet. Den förnybara gasen idag produceras huvudsakligen via rötning, men innefattar även metan från termokemisk omvandling och vätgas via el som produceras i temporära överskott från sol eller vindkraft. Metan från skogsavfall demonstreras i Göteborg och den andra typen av förnybar vätgas demonstreras på många ställen, bland annat i Tyskland.**

I denna framtida situation kommer det, till skillnad från dagens situation, att finnas ett mycket större antal inmatningspunkter på gasnäten. I Sverige har det historiskt bara funnits en inmatningspunkt i Klagshamn, där gasnätet når Sverige, vilket också reflekteras i hur gaskvaliteten bestäms i nätet idag. Men med en framtida situation med multipla inmatningspunkter på både transmissionsnät och distributionsnät uppstår ett behov av att kunna mäta och säkerställa kvaliteten på gasen som levereras till slutkund. Denna rapport försöker dra nytta av erfarenheter från andra europeiska länder där detta problem, i alla fall delvis, adresserats och försöka föreslå en rimlig väg framåt för det svenska gasnätet. De länder som legat till grund för studien är Tyskland, Danmark och Nederländerna samt en ISO-standard på området.

Informationen i det genomgångna materialet från andra länder kan delas in i fyra delar. Den första delen presenterar olika typer av gasnätskonfigurationer medan den andra delen går igenom olika aspekter av mätning så som mätfrekvens, mätnoggrannhet, precision och kalibrering. Den tredje delen beskriver olika metoder för allokering av värmevärde i olika nät medan den sista delen går igenom procedurer för kontroll av värmevärdesallokering.

Den tyska och danska standarden är relativt detaljerade med avseende på värmevärdesallokering medan den holländska standarden nämner det kortfattat. Den ISO-standard som finns ger ingen speciell information om själva utförandet utan konstaterar bara att det måste göras.

För att få till en bra metod för att mäta och säkerställa kvaliteten, framförallt med avseende på värmevärde, i det svenska gasnätet bör ett system för validering och övervakning av densamma utvecklas gemensamt av branschens parter. Dock måste en överblick av de framtida intressanta nättyperna först erhållas. Som en rekommendation skulle det svenska samarbetet följa den danska modellen där en tredje part är ansvarig för validering och säkerställande av kvaliteten.

## Summary

**When there is more renewable gas being produced, and exported to the natural gas grid, there is a new situation for the grid operators which, in extension, creates new circumstances with respect to measuring and ensuring the gas quality on the grid. The renewable gas is today mainly produced by anaerobic digestion, but near-term future sources may be methane from thermochemical conversion of lignocellulose and hydrogen produced from intermittent electricity stemming from wind and solar resources; indeed, the first type of gas is currently demonstrated in the Swedish context in Gothenburg and the second type in Germany.**

In this future situation, there will, in contrast to today's situation, be a much larger number of feeding points to the grids. In Sweden, there has historically been only one feeding point, something that is reflected in the way the gas quality is currently determined in the grid. However, with more renewable gas on the grid, the quality of the grid has to be monitored in a more controlled and detailed manner. This report will try to draw upon the experience from other European countries where this problem has been addressed already and try to suggest a reasonable way forward for the Swedish gas grid. The countries assessed is Germany, Denmark and the Netherlands as well as the ISO standard on the subject.

The findings in the reviewed material from the countries listed above have been divided into four parts. The first part present different type of gas grid configurations. The second part present information regarding measuring procedures, including guidelines for measuring frequency, accuracy and calibration. The third part describe different methods for allocation of calorific value in different grids. The last part present procedures regarding control of allocated heating values.

The German and Danish standards are quite detailed with respect to allocation of heating value. The Dutch document reviewed mainly pertain to biogas feeding to the grid, allocation of heating value is mentioned briefly. Finally, the ISO standard is non-specific on deciding in allocation-method, it is more exemplary in nature.

Guidelines for validation and supervision of the calorific value in the Swedish gas grid should jointly be developed by the actors of the Swedish gas industry when a clear view of what different types of gas grids will be of interest is obtained. A suggestion is to follow the Danish model and assign to a third party the responsibility of validation and supervision.

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# 1 Introduction

Natural gas is not one of the main energy sources in the Swedish energy system. It is however a very important energy source for many customers – industrial, residential, and others – in the southwestern part of the country. These customers rely on the ability of the grid to supply natural gas of high quality to meet the demand. The quality of the gas in the Swedish natural gas grid does show variations with time. Gas quality does in this context mainly refer to the calorific value (or heating value) of the gas, which in turn depends on its composition [1,2]. It is highly likely that these variations will become more frequent, and larger in amplitude in the future.

There are multiple factors contributing to current and future variations in the quality of the supplied gas. The main part of the gas in the Swedish transmission grid is Danish North Sea gas, a natural gas of high and relatively constant quality [3]. The Swedish natural gas grid was up until 2011 only supplied with North Sea gas but is today, due to declining production and periods of no production in Denmark, supplied with German gas via the Danish pipelines. This gas is of a lower quality, i.e. it has a lower calorific value, than the Danish North Sea gas. Due to increasing integration of the European natural gas grids and energy markets – which is one of the policy areas that are prioritized by the European commission as the Energy Union – as well as global international trade of natural gas, it is becoming increasingly plausible that Sweden will be provided by additional gas of varying quality produced in other European countries. Apart from pipeline connections to exporting countries, the Swedish gas grid can also be supplied with gas from shipping terminals for imported liquefied natural gas. In addition to the variations in the gas that is being imported, increasing volumes of domestically produced biogas and substitute natural gas (SNG) from biomass gasification, which both have different qualities compared to conventional natural gas, are being fed into the grid. The interest for power-to-gas technologies is also increasing, pointing to yet another possible, future source of gas that could find its way to the Swedish gas grid. All these supply options lead to variations in gas composition. Without adjustment, these variations will lead to a differentiated calorific value, which will depend on time and location, throughout the Swedish transmission and distribution grids.

These increasing variations pose a problem in quality control and debiting, an issue that is well known by the actors of the gas industry and which has previously addressed in several reports on behalf of Svenskt Gastekniskt Center (currently Energiforsk, the Swedish Energy Research Centre) and Energigas Sverige [1–3]. Swedegas also publishes real-time information about gas quality on their website to inform about the current status. End users can receive gas of different quality at different point in time and calorific value measurements and debiting must be adapted to these variations. To date there is no framework in place in Sweden that deals with calorific value control in grids with multiple feeding points of varying gas quality. Trading with natural gas in Sweden is primarily regulated in the Swedish law on natural gas (SFS 2005:403 [4]) and the specified regulations on measuring and reporting of traded natural gas (EIFS 2014:8 [5]). The Swedish gas



industry has also adopted internal guidelines (“Gasmätning – Anvisningar för den svenska energibranschen” [6]) which however currently not adequately describe what methods for measurement and allocation of calorific values and what procedures for quality control are acceptable to use.

### 1.1 AIM

The aim of this report is to present (i) an overview of the literature on how to handle variations in gas quality in gas grids, (ii) how gas quality variations is being regulated and handled in other European countries, and (iii) discuss possible ways of dealing with these issues in Sweden.

This report presents results from the project “Measuring and ensuring the gas quality of the Swedish gas grid”, which is a part of a collaboration within the Swedish gas industry aiming to develop a national regulatory framework for gas quality. The results from this report will serve as underlying material when developing the national regulatory framework regarding aspects such as determination of calorific value and quality control.

### 1.2 METHOD

Information regarding measurement methods and regulatory frameworks that already are in place in countries with gas grids with varying gas quality has been compiled and reviewed. Relevant agencies in multiple European countries were contacted and asked to provide information regarding regulations connected to varying calorific values. The reviewed material has been collected from Denmark, Germany, Netherlands, Sweden and current ISO standards.

The compiled information has been reviewed by a workgroup consisting of representatives from actors of the Swedish gas industry and academia. Representatives from E.ON, Kraftringen, Lund University, Swedegas and Öresundskraft participated in the work group. The purpose of the workgroup was to prepare a proposal for what changes and additions should be made to the current Swedish industry-wide gas measurement guidelines to accommodate for variations in gas quality.

### 1.3 DEMARCATIONS

No material from outside of Europe has been collected. Other natural limitations to the scope of the literature search has been language. The literature search has been limited to Swedish, English, Danish, German, Polish and Dutch.

No revision of the current guidelines and regulations has been made. The reviewed material has simply been compiled and solutions for the Swedish market are presented based on existing material.

## 2 Gas use and quality in Sweden

### 2.1 THE SWEDISH GAS GRID

The foundations to the Swedish gas grid were laid in 1985 [7]. It consists of a transmission grid that spans from Trelleborg to Stenungsund, about 600 km pipelines, and multiple distribution grids, in total about 2800 km pipelines, that supply numerous municipalities along the transmission grid with gas, Figure 1. About 37,000 Swedish costumers, of which 34,000 are residential, are supplied with energy for heating and cooking. The remaining costumers are industrial plants and district heating companies [7]. In addition to the gas grid, local distribution grids which are not connected to the transmission grid exist, e.g. in the city of Stockholm. More information about the Swedish gas grid can be found in Nelsson, 2011 [2].



Figure 1. Swedish gas grid [8]

Today, most the gas in the Swedish transmission grid is supplied from Denmark via one single feeding point in Klagshamn south of Malmö. This feeding point is believed to remain the only external feeding point for the foreseeable future. In addition to the external feeding, the transmission grid is also fed by gas from the gas storage in Skallen in Halland, by GoBiGas in Gothenburg and by Jordberga in Trelleborg. Also, a LNG terminal which might be used for supplying the transmission grid may be constructed in Gothenburg. The LNG facility is part of a future and more extensive project involving the construction of an LNG terminal at the Port of Gothenburg. The terminal will also be connected to the transmission grid to supply shipping, the transport sector and industry with LNG. On the

distribution grid level, smaller amounts of biogas are also being mixed into the natural gas. The calorific value of the gas in the grid is currently being measured in Dragør in Denmark before entering Sweden, in Årstad in Halland, in Råvekärr south of Gothenburg and in Kålsered north of Gothenburg. These existing points of measurements will not be sufficient to predict an accurate calorific value for all end users when the expected variation in gas quality in the grid start to increase.

## 2.2 USE OF GAS IN SWEDEN

The Swedish gas grid currently transfers around 10-11 TWh natural gas annually, depending on the energy demand during winter [7,9]. This corresponded to about 2% of the total energy supply in Sweden. However, there are large regional differences that are dependent on the location relative to the gas grid. In municipalities in the south and west of Sweden which are connected to the gas grid, natural gas accounts for 20-25% of the primary energy supply [7,9]. This is at the same level as in the rest of Europe. Table 1 contains the total energy supply for Sweden 2014.

**Table 1. Total energy supply in Sweden 2014 [10]**

<b>Commodity</b>	<b>TWh</b>	<b>%</b>
Biomass	130	23%
Coal and coke	21	4%
Crude oil and oil products	134	24%
Natural gas, gasworks gas	9	2%
Other fuels	14	3%
Nuclear fuel	182	33%
Primary heat	5	1%
Hydropower	64	11%
Wind power	11	2%
Import-export of electricity	-16	-3%
<b>Total</b>	<b>555</b>	<b>100%</b>

Most of the gas consumed in Sweden is consumed in the region of the gas grid, but there are also smaller amounts of LNG being imported, mainly from Norway, to other regions. Figure 2 display the natural gas use by sector from 1983 up to 2014. At present day, the two largest areas of use for natural gas in Sweden are as fuel for electricity and heat production, and use in industry. The peak in 2010 is a result of investments made in gas-fired combined heat and power in combination with a cold winter. The third largest area of use is the residential and service sector where gas is used for heating and cooking purposes. The remaining two areas are as

vehicle fuel in the transport sector and as raw material in industry (non-energy use).

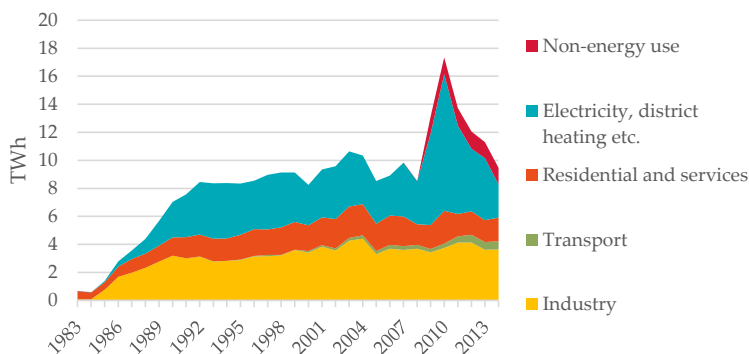


Figure 2. Natural gas use in Sweden by sector 1983-2014 [10]

Looking at projections made for 2016-2018 it is believed that the natural gas use will increase slightly as an increasing amount of companies in different sectors replace oil with natural gas [11].

### 2.3 VARIATIONS IN GAS COMPOSITION AND QUALITY

Variations in gas quality can arise due to production related and technical causes [1]. Production related variations are due to fluctuations in the gas field where the gas is produced, i.e. the composition of gas extracted from a certain field will change slightly. These variations occur over years and decades and do not cause any sudden, large variations in grid gas quality. The Danish gas, which constitutes the majority of the gas in the Swedish grid, has for example had a slightly decreasing content of methane and increasing content of heavier hydrocarbons (mainly ethane and propane) over the last 25 years. The average methane content over the last ten years has however been quite stable at around 90 % according to statistics from Swedegas. Technical variations however can be large and sudden and are what may affect end users both technically and economically. These variations may for example occur when gases produced at different gas fields are mixed in the grid, or when gas from a new source is being fed into the grid, e.g. German gas.

The composition of gas entering the Swedish gas grid is monitored and the statistics are made available by Swedegas. Knowledge of the composition allows for the quality of the gas entering the grid to be determined. Figure 3 shows the variations in gas composition and associated variations in calorific value as monthly averages over the five-year period from 2011-2015. As shown in the figure there are fluctuations in the gas composition, but no clear trend can be discerned over the five-year period.

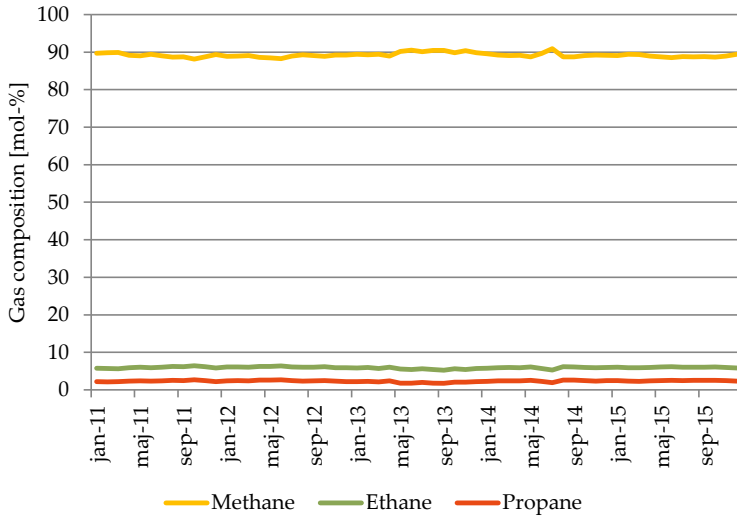


Figure 3. Gas composition over a five-year period. Data from Swedegas [12].

Figure 4 show the gas quality, i.e. higher heating value, varied over the year 2015 using available statistics for daily and monthly average values. This shows that although the variations in the gas composition may be small, these variations result in rapid changes in gas quality. The yearly average for 2015 was 12.155 kWh/Nm<sup>3</sup> with a standard deviation of 0.049 for the daily average values and 0.032 for the monthly average values, i.e. 0.40 % and 0.26 % for the daily and monthly averages respectively.

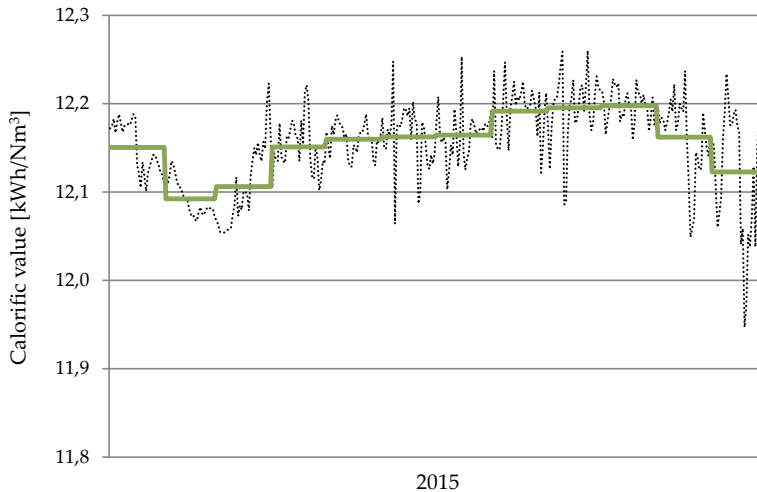


Figure 4. Variations in gas quality during 2015. Data from Swedegas [12].

Over the last couple of years, there has been an increase in the injection of upgraded biogas and SNG to the gas grid. Figure 5 displays the injection capacity by region for the years 2008-2015 [13–20].

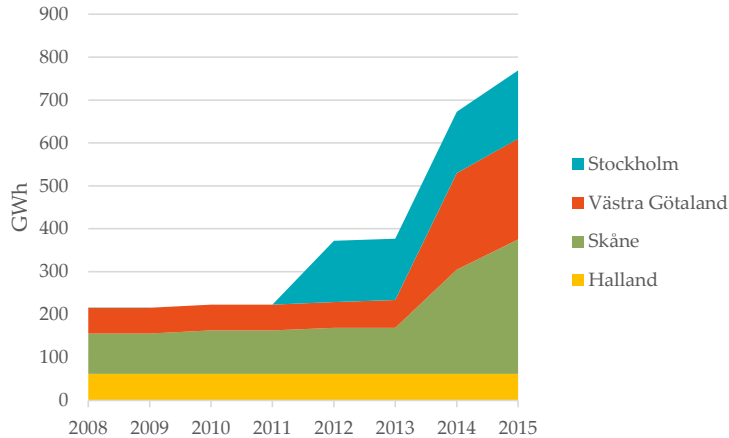


Figure 5. Injection capacity of upgraded biogas and SNG to the gas grid 2008-2015 [13–20]

Injection data before 2008 is not available and injection data for Stockholm is only available from 2012; please note that Stockholm is not connected to the main Swedish natural gas grid but a local grid. Important to note is that the reported figures only show injection capacity, not the actual injected volume at the time. The large increase in injection capacity that occurred in 2014 is due to the injection start for GoBiGas in Västra Götaland and Jordberga in Skåne. Injected volume compared to injection capacity is shown in Figure 6.

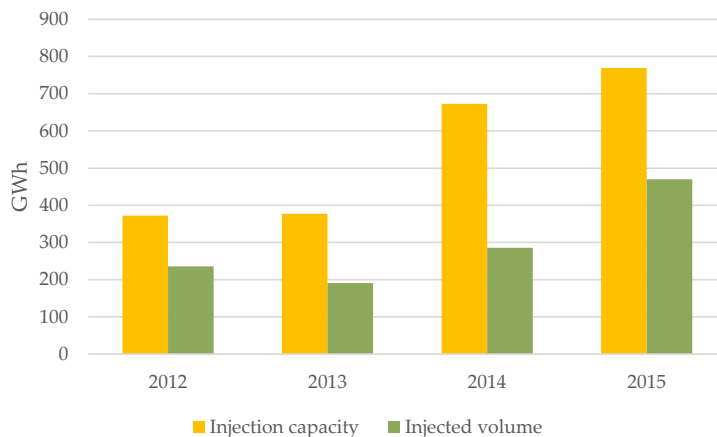


Figure 6. Injection capacity and injected volume of upgraded biogas and SNG to the gas grid 2012-2015 [17–20]

Currently SNG is only being injected on a transmission grid level. Biogas however is being injected both to the transmission grid and directly into distribution grids. Looking at the Swedish situation, GoBiGas is projected to deliver 160 GWh of SNG annually to the transmission net which will contribute to a significant change in gas quality around Gothenburg [3]. Similarly, the grids surrounding Jordberga will be affected by the annual production of 120 GWh of biogas from anaerobic digestion. In addition to these two inputs, there exist about 10 additional anaerobic digestion plants, which deliver biogas to local distribution grids. On a distribution-grid level, direct injection of biogas can lead to end users getting either pure biogas, pure natural gas or a mixture of both depending on location in the grid, gas consumption rate depending on season and production rate. The quality of the different gas streams is thus of great importance to avoid unjust debiting.

The quality of new gas sources differs from that of the conventionally used natural gas. Upgraded biogas that is being added to the gas grid consists of 97% methane and 3% inert gases. As previously mentioned, the natural gas that is being imported into Sweden contains higher hydrocarbons, which are not found in upgraded biogas and SNG. These higher hydrocarbons have a higher calorific value compared to methane, which leads to natural gas having a higher calorific value than upgraded biogas and SNG. Gas produced with power-to-gas technology consists either of hydrogen or pure methane [21], and thus also has a lower calorific value than the currently sourced natural gas.

One option to circumvent the issue of injecting gas of lower quality into the grid is to homogenize the calorific values by increasing the calorific value of upgraded biogas and SNG before injection. This is done by adding propane to the gas, a process known as propanation. This method is currently in use for all biogas in Sweden that is fed into the transmission grid [3]. The ideal situation would be to make real-time adjustment of the calorific value; however, this is rarely possible as different actors are responsible for the determination of the calorific value of the different gas streams. Instead, the calorific value of the upgraded biogas and SNG is adjusted to the monthly average of the previous month. Downsides to propanation are the extra costs incurred for the producers of biogas and SNG as well as the fact that the propane is fossil (at least at this time, renewable alternatives are in development), meaning that the potential for GHG reductions from biogas production is reduced. Implementing regulations for multiple feeding point grid with multiple gas qualities would open up the possibility to skip propanation.

## 2.4 ISSUES WITH VARIATION IN GAS QUALITY

Variations in gas quality may affect the end users both technically and economically. Possible technical complications in equipment running on natural gas due to variations in quality will not be covered in this report. However, the subject has previously been discussed in published reports [1–3]. It can be mentioned that no clear correlation between changed technical performance and gas quality could be found. The economic effect is considerably more tangible. The current debiting system is based on the amount of energy an end user has consumed. This amount is calculated as the product of gas volume that has been

consumed by the end user and the monthly average calorific value that is assigned to the end user [3]. Quality variations in the grid means that the end user may receive gas of different quality during the same settlement period. Measurement and debiting has to be adapted to this possibility to avoid unjust debiting.



### 3 Earlier research

Even though the simulation of multiple feeding points of various grids are common practice, especially for electricity, indeed there are large government programs in several regions on this topic as well as commercial software developed [22–24].

The same approach with simulation of net-impact with respect to gas grids is not as well investigated. This is not to say that there is no simulations performed on gas grids, this is not the case. There are many papers dealing with different problems in natural gas handling as shown by a recent extensive literature review [25]:

1. Short term basis storage
2. Pipeline resistance
3. Compressor station modelling

The impact on gas quality with respect to multiple point injection is however a question that is increasing in relevance with increasing renewable content on the gas grid, as well as the entry of power-to-gas technology into the market. There are of course studies performed on this so called pooling problem [25,26] but it is mainly concerning general mixing of gases with varying quality and how to solve the problem from a mathematical standpoint. The mathematical model includes bilinear and multi-convex quadratic programming (quality) constraints [27,28].

There are studies on the combined optimization of different grids, e.g. natural gas and electricity (in particular with renewable electricity sources) [29,30]. In a paper by An et al. [31] the fundamental modelling of the natural gas grid was performed and, in the modelling work, also the transformation between gas and electricity (generators) were included. In the study, the modeling showed that considering both grids in the same model lead to social welfare maximization and that the power generation was sensitive to wellhead gas prices. However, this, and other, studies [29,31] are based on the steady-state Weymouth equations [25] that are unable to catch the dynamic effects in the grids causing changes on a less-than-one-day timescale. This is naturally mostly important when the natural gas grid used with gas turbines to cover mid-meridian electric demand.

The problem to date has however only been uni-directional, producing electricity from gas and how the variation in the electricity generation is influenced by the intermittent generation of renewable electricity. With the advent of more power-to-gas applications, there is a more complex situation as the new bi-directionality of the two energy vectors is also to be considered. To summarize the problem [32]:

“The grid could start receiving several different gases, whose properties variations (heating value, density) could significantly influence the management of the grid”

The injection of different qualities of gas at different points along the gas grid will cause issues. In particular, when there are large differences in properties between the various gases injected. This is best illustrated when injecting hydrogen in the gas grid. A study on injecting hydrogen on the Italian gas grid, as a power-to-gas

play, was recently published by Guandalini et al. [32]. The study reveals that there is first of all an effect of the injection on the Wobbe index and the heating value, which is to be expected. However, what is more unexpected is the dynamic effects on the hydrogen concentration. This parameter, largely, depend on the user profile and out-take along the pipeline. In addition, the simulations performed in the paper shows that there is a need for moving away from traditional, volumetric measurement of the delivered gas and to base the measurement on energy instead.

As mentioned before, the quality of the gas on the grid has been calculated using simulation models in many instances. The transmission gas grid in Germany has had quality tracking using software for decades [33]. However, using quality tracking software for the distribution grid has until recently been difficult due to the much larger number of input/outputs in these grids, also there may be multiple feed-in points complicating the calculations further.

There are a few commercial software for sale with Simone [34] and PSIGanesi [35] being a well-used ones, as well as the SmartSim software developed by E.ON [36–38], which appears to be more suitable to distribution grid simulations. The purpose of the quality tracker is to ensure the correct debiting information to the end-user such that the bill reflects the received heating value of the gas. In designing and developing these software, an important parameter is to describe the theoretical user consumption profiles. These consumer profiles have been thoroughly researched by Hellwig and is used in many of the papers and publications on the qualification of quality tracker software [36,37,39].

Much of the current work is aimed at improving the software calculation routines and verifying the use of the SmartSim software with real-life examples [36–38]. Several grids in Germany, Denmark and Sweden have been investigated during the 2014-2016 timeframe and the deviations between the SmartSim software and actual grid composition has been measured. In some cases the software has been implemented [38].

As mentioned much attention has been put on the uncertainty of the calculations of the gas quality in different points in the grid using the quality trackers. Kessel and Sommer [33] evaluated the validity of a quality tracker which was based on the guidelines from ISO on uncertainty of measurement and in particular the 1st supplement focusing on propagation of distributions using Monte Carlo simulations [40,41]. Their findings are quite clear in that for the most part the quality tracker performs really well in describing the chosen (simulated) grid. By giving input ranges and distribution functions for a range of parameters (Table 2), the variations in quality in different nodes has been simulated.

**Table 2. Specification of knowledge for input quantities [33]**

<b>Input</b>	<b>Knowledge precision</b>	<b>Distribution</b>
Calorific value	< 1%	Normal
Source flow rate	< 2%	Rectangular
Drain flow rate	< 2%	Rectangular
Grid ref. pressure	< 5%	Rectangular
Temperature	0-15 °C	Rectangular
Length of pipes	< 10%	Rectangular
Diameter of pipes	< 5%	Rectangular
Roughness	< 50%	Rectangular

In some instances, the error was low (< 2.5%) and for a majority of the pipelines and flows the uncertainty was below 30%. However, in some cases, amplified by large diameter pipes with low flowrates, the errors may be as high as 300%. However, despite the errors in flowrate, the variation in the calorific value only varied by a maximum of 5% and the conclusion was drawn that the modelling was good enough for debiting purposes (with averages over 1 month), but that real measurements had to be performed to validate the model.

## 4 Findings from the comparative analysis

The findings from the reviewed material from other countries have been divided into four sections. In the first section, different types of gas grid configurations are presented. The second section contains information regarding measuring procedures, including guidelines for measuring frequency, accuracy and calibration. In the third section, different methods for allocation of calorific value in different grid types are described. Lastly, procedures regarding control of allocated heating values are presented. The Danish (Naturgasselskabernes kontrolmanual for allokering af brændværdi i distributionsnettet [42]) and German (Technische Regel Arbeitsblatt G 685 [43]) standards are quite detailed with respect to allocation of heating value. The Dutch document reviewed (Richtlijnen beheersprotocol groengas invoedingen [44]) mainly pertain to biogas feeding to the grid, allocation of heating value is mentioned briefly. Finally, the ISO standard (Natural gas - Energy determination ISO 15112:2011 [45]) is non-specific in deciding in allocation-method, it is more exemplary in nature.

### 4.1 GAS GRIDS

This section gives an overview of the configurations and strategies for calorific value allocation in both single and multiple feeding point distribution grids. The graphic symbols used when displaying gas grids are explained in Figure 7.

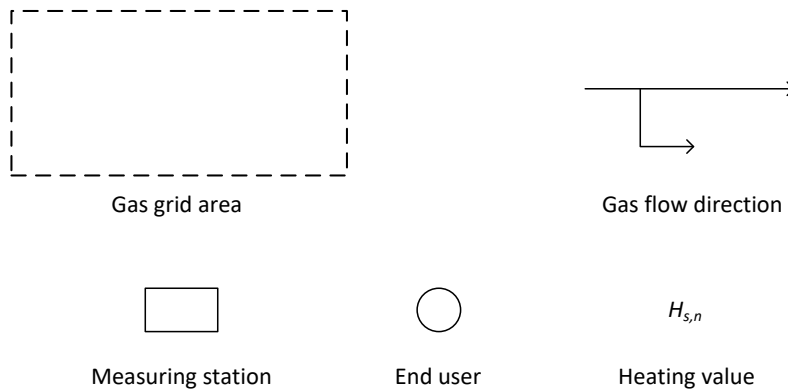


Figure 7. Gas grid graphic symbols

#### 4.1.1 Distribution grids with single feeding point

Most common for distribution grids with only one feeding point is that the calorific value of the gas that has been determined before the transition from the transmission to the distribution grid is assigned to the entire distribution grid. There are, however, exceptions where multiple calorific values exist in a distribution grid with single point feeding.

The first exception is when an end user has access to equipment to measure the calorific value [42]. In this case that end user is assigned the self-measured calorific value regardless the value that is assigned to the remaining end users in the same distribution grid, Figure 8.

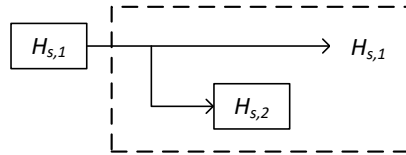


Figure 8. End user with calorific value measuring equipment

The second exception is when there locally in the distribution grid exists equipment to measure the calorific value [42]. In this case the distribution grid is divided into multiple zones where the zone upstream from the measuring equipment is assigned the calorific value determined before the transition from the transmission to the distribution grid and the zone downstream from the measuring equipment is assigned the locally measured calorific value, Figure 9.

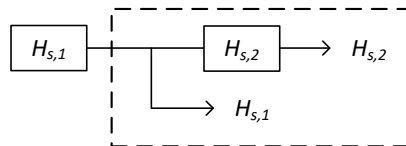


Figure 9. Grid with local calorific value measurement

#### 4.1.2 Distribution grids with multiple feeding points

The task of allocating calorific values in a distribution grid gets increasingly complicated when the number of feeding points increase. This is especially true if the feeding points supply gas of different quality. There are two types of distribution grids with multiple feeding points.

In the first type of distribution grids with multiple feeding points the incoming gas is mixed before reaching the end users [45], Figure 10.

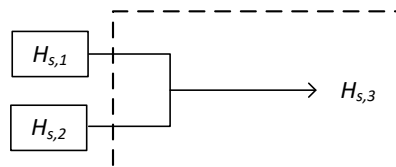


Figure 10. Gas grids with multiple feeding points with gas mixing before end users

Depending on how the feeding is configured it is sometimes possible to allocate a set calorific value for the entire distribution grid that coincides with one of the ingoing values. This can be done if transportation time within the grid is disregarded and the following criteria are met:

- Each individual feeding point has the capacity to supply the entire distribution grid independent of the others
- Only one feeding point at the time is in operation at any given moment
- The time span the different feeding points are in operation is being documented

If these criteria are not being met, then the calorific value for the distribution grid should be calculated or otherwise determined.

In the second type of distribution grids with multiple feeding points the incoming gas is not mixed before reaching the end users [42,43,45]. Mixing instead occurs at the end users, Figure 11. In this case, it is possible that some end users only are supplied by gas from one feeding point while other end users are located in a mixing zone.

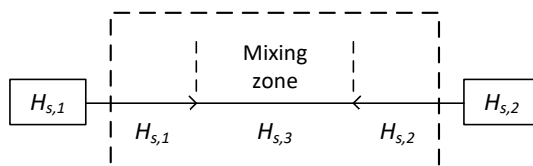


Figure 11. Grid with multiple feeding points and gas mixing at end users

It is possible to assign one calculated calorific value for the entire distribution grid but this should be avoided if incoming calorific values differ significantly from each other as it will lead to unjust debiting for some end users. Instead, in the case of large differences in incoming calorific values, the distribution grid should be divided into smaller calorific value zones where zones close to a feeding point is given the calorific value of that point and zones in mixing zones are given a calculated or otherwise determined calorific value. For very complex distribution grids with a great number of feeding points or large variations in incoming calorific value a state simulation tool known as a Quality Tracker (Section 4.3.3) should be considered.

## 4.2 MEASURING PROCEDURES

The general recommendations found in the reviewed material state that existing ISO standards and national regulations regarding measuring equipment and procedures are to be used if these types of documents are available. However, it is important to ensure that the entire national gas industry use the same standards and regulations as to avoid systematic differences in results between different actors. The most common method for determining the calorific value in Sweden is through gas chromatography but direct measurement is also used, see Section 4.3.1 for more information.

Examples of international standards that have been referred to in the reviewed material [45,46,44]:

- ISO 6974 1-6: Natural gas – Determination of composition with defined uncertainty by gas chromatography [47]
- ISO 6975:1997: Natural gas – Extended analysis – Gas-chromatographic method [48]
- ISO 6976:2016 Natural gas – Calculation of calorific values, density, relative density and Wobbe indices from composition [49]
- ISO 10715:1997 Natural gas – Sampling guidelines [50]
- ISO 15971:2008 Natural gas – Measurement of properties – Calorific value and Wobbe index [51]

In addition, there are several supporting ISO standards regarding calibration gases, evaluation of analytical systems, volume conversion, density, pressure and temperature, etc.

#### 4.2.1 Measuring frequency

To obtain a representative calorific value several measurements within regular intervals have to be carried out. The obtained measurements are used to calculate a representative average for the settlement period, this to minimize the influence of possible outliers. Germany uses hourly measurements and the values are then used to calculate a daily average [43]. Monthly averages are then calculated from daily averages, monthly from daily, etc. Danish regulations specify that hourly measurements are to be used if available, otherwise daily measurements are used instead [42].

In the Dutch biogas manual it is specified that the Wobbe index of biogas should be measured on an hourly basis but do not mention any frequency for the calorific value [44]. No recommendations for measurement frequency is given in the ISO standard, however it is recommended that more frequent measurements should be performed the more the calorific value varies [45].

#### 4.2.2 Measurement accuracy

Existing ISO standards contain specifications on what level of measurement accuracy is required for the standard to be valid. As all the national regulations that have been reviewed either build on or refer to ISO standards, it is safe to assume that the requirements on measurements accuracy found in the national regulations are based on the requirements set in these standards. As an example the maximally allowed deviation for calorific value measurement is set to  $\pm 0.5\%$  in Denmark while the Netherlands use  $\pm 0.4\%$ . These values are with high likelihood based on what accuracy can be reached when using ISO standards ISO 6974 and ISO 6976. The German standard contains nothing on measuring accuracy in the standard for the natural gas grid heating value allocation. There are however good recommendations for assessing error propagation in measurement and calculations provided by the joint Committee for Guides in Metrology, which are quite helpful in understanding this propagation problem in measurement [40,41].

### 4.2.3 Calibration

Existing ISO standards contain calibration procedures that must be fulfilled for the standard to be valid. The general instrument calibration procedure is to validate a known value of the parameter studied (calorific value, gas composition, etc.). If the measured value falls outside the maximally allowed deviation specified for the instrument, then a calibration of the instrument must be carried out whereupon a new value validation is performed. This procedure is repeated until the measured value falls within the maximally allowed deviation. The national standards are slightly more specific and the German standard mention calibration guidelines on page 10 ("Gesetz über das Mess- und Eichwesen (Eichgesetz – EichG)") [43]. The Danish standard refers to the instrument manual, which may contain specifications for calibration [46]. The Dutch standard is the most demanding and say that P, T and volume flow instruments should be calibrated according to manufacturer instructions and that gas chromatographs should be validated/calibrated once a week [44].

## 4.3 ALLOCATION OF CALORIFIC VALUE

There are various methods available determination of calorific values viable to use when debiting end users. Which method to use mostly depends on the configuration of the affected gas grid and on what resources are available. This section gives a presentation of the various methods found in the reviewed material.

### 4.3.1 Direct measurement and gas chromatography

The calorific value of the gas can be determined either by direct measurement or by being calculated from the gas composition obtained by gas chromatography [45,44]. Both methods are carried out in accordance with existing ISO standards referred to in Section 4.2. Also, ISO standards regarding representative sampling and gas chromatography analysis are also of relevance when performing calorific value measurements. Calorific values that have been obtained by either of these methods can be used directly for debiting purposes in single feeding point grids, see Section 4.1.1.

It seems that gas chromatography is the preferred method; Denmark has a specific gas chromatography manual [46] and both the German and Dutch documents mention the use of ISO 6976. However, the Dutch document also state that additional methods for determining the calorific value are allowed as long as it can be proven that the method is accurate enough [44]. The ISO standard list multiple methods but do not give any recommendations on which one to use [45].

### 4.3.2 Flow-weighted calorific value

When multiple gas streams of different quality are mixed a flow-weighted calorific value can be calculated for the gas downstream from the mixing point. The flow-weighted calorific value is calculated using the calorific values ( $H_{s,n}$ ) and flows ( $Q_n$ ) of the incoming gas streams according to:



$$H_s = \frac{\sum_{i=1}^n H_{s,i} \cdot Q_i}{\sum_{i=1}^n Q_i}$$

This method to determine the calorific value can be used to allocate calorific values to grids with multiple feeding points (Section 4.1.2). However, this method should only be used for simpler grids as the risk of unjust debiting increases with increasing grid complexity. More complex grids should be divided into smaller calorific value zones to increase allocation accuracy. Below follows two examples.

**Example 1:** Gas grid with two feeding points and one calorific value zone [42,45]

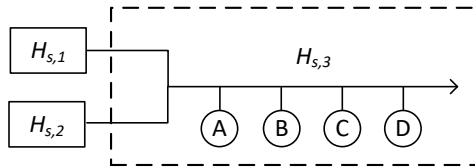


Figure 12. Gas grid with two feeding points and one calorific value zone

The grid is fed by two feeding points with different calorific values simultaneously. As mixing of the gas streams takes place before reaching the end users a flow-weighted calorific value can be assigned to the entire grid. The flow-weighted calorific value is calculated as:

$$H_{s,3} = \frac{H_{s,1} \cdot Q_1 + H_{s,2} \cdot Q_2}{Q_1 + Q_2}$$

**Example 2:** Gas grid with two feeding points and three calorific value zones [42,43,45]

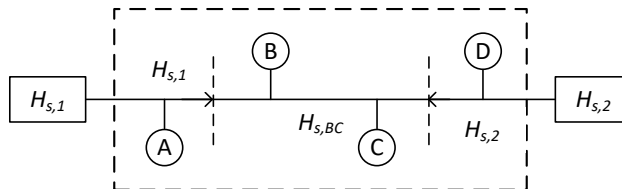


Figure 13. Gas grid with two feeding points and three calorific value zones

In the case where an end user is located close to a feeding point where the flow in the grid significantly exceeds the consumption of the end user, it can safely be assumed that the calorific value for the end user coincides with the calorific value of the feeding point. In this example end user A receives gas with the calorific value  $H_{s,1}$  provided that  $Q_1 \gg Q_A$  and the corresponding reasoning applies to end user D. For end users B and C however a flow-weighted calorific value has to be calculated according to:

$$H_{s,BC} = \frac{H_{s,1} \cdot (Q_1 - Q_A) + H_{s,2} \cdot (Q_2 - Q_D)}{(Q_1 - Q_A) + (Q_2 - Q_D)}$$

### 4.3.3 Quality Tracker

A Quality Tracker (QT) is a state reconstruction tool that allows the user to calculate calorific values at any point in a gas grid using incoming calorific values, gas volume flows and standard load profiles for end users [45,52]. QT have been used in e.g. Germany to track the calorific value in transmission grids for several years and new QT systems that can be applied on distribution grids have recently been developed. A detailed description can be found in [52]. This tool is especially useful in complex grids where the accuracy of the flow-weighted calorific value is insufficient such as grids with several feeding points, with large variations in flow and/or incoming calorific values and in grids where there for some reason is not possible to measure the calorific value. Examples of model input are found in Table 3.

**Table 3. Specification of knowledge for input quantities**

Input information	Data source
Calorific values at entry points	Measured values (verified)
Normal volumes at entry points	Measured values (verified)
Normal volumes at exit points	Measured values (RDM customers); SLP data corrected on the basis of volume balance*
Network pressures	Pressures measured at representative points
Topology data (such as line lengths, line diameters, surface roughness)	Data obtained from network operator

\*RDM customers: customers with recorded demand measurement. SLP customers: customers whose energy consumption is determined using standard load profiles

At this current time there is no detailed documentation available regarding the use of QT. QT is mentioned in the Danish regulations and in ISO 11512 but no further information is given. The German standard DVGW Arbeitsblatt G685 however is under revision and the new edition will also include regulations regarding the use of QT.

According to DONG in Denmark there is currently no regulations in place for the use of QT [53]. However, the Danish system is well on its way to submit a proposition for the implementation of QT regulations where the underlying information for the proposition has been obtained from Germany. The proposition will demand that controls of the calorific value shall be carried out annually at representative checkpoints where the QT calorific value is compared to a measured one. In both Denmark and Germany the maximal allowed deviation between measured and calculated calorific is set to 2%, see Section 4.4.1 for more information. Additional controls of the calorific value will be carried out when larger changes are made to the grid. Large changes are changes in gas flow larger than 10% and grid reconstruction where the physical length of the pipes change with more than 10% [53].

#### 4.3.4 No determination of calorific value in grids with multiple feeding points

There are scenarios for grids with multiple feeding points where no determination of the calorific value in the grid is needed. Looking at grid configuration, the scenario of a grid with multiple feeding points where mixing of the gas takes place before reaching the end users but where each individual feeding point has the capacity to supply the entire distribution grid independent of the others, described in Section 4.1.2, is an example where no new calorific value determination has to be performed locally. Another example is grids with multiple feeding points where mixing of the gas takes place at the end users but where there exist zones where some end users clearly only receive gas from one feeding point based on volume flows. These zones can be assigned the calorific value of their correspondent feeding point, see Section 4.3.2, Example 2.

Additional situations where determination of calorific value might be considered unnecessary due to the relations of the incoming gas qualities and volumes exists. One example is when the incoming calorific values do not differ significantly from each other. In this case it might be acceptable to use the lower calorific value for debiting in the entire grid. Another example is when a local biogas producer occasionally delivers a small volume of biogas with a low calorific value to a significantly larger gas flow. In this case the impact of the added biogas volume is small enough to be disregarded and the calorific value of the larger gas flow is used for debiting.

Regardless what grid configuration or gas feeding scenario is under consideration a sensitivity analysis should be carried out to estimate what variation and/or deviation in calorific value might be expected. If the variation and/or deviation is deemed to be insignificant then the option of not determining new calorific values continuously may be considered.

#### 4.3.5 Absent calorific value

Due to various reasons, e.g. faulty measurement equipment or ongoing service, it may occasionally occur that no calorific value is measured or delivered to a grid during a limited period of time. The German regulations and ISO 11512 state that a substitute calorific value may be used or is required for debiting during these periods [45,43]. Neither the Danish nor the Dutch regulations contain information regarding substitute calorific values. Substitute calorific values should only be used if no correctly operating measuring equipment is available and all involved grid actors agree that it should be implemented. Also, according to ISO 11512, all affected end users must be informed of that a substitute calorific value is in use and should also be informed of what method was used to determine it [45].

##### *Methods for determining substitute calorific values*

There are different suggested methods for how to determine a substitute calorific value. Different methods might be more appropriate to use depending on situation and length of the period when the substitute calorific value is to be used. Suggested methods are:

- Redundant measuring equipment

- Calorific values from up or down stream located measuring equipment
- Interpolation between last know and newest calorific value measurement
- Reuse of latest calorific value
- Comparison with historic values from similar period

#### 4.4 CONTROL

In addition to measuring and allocation strategies there is also a need for control procedures to ensure that the end users are indeed debited for the correct calorific value. This entail regular periodic control of allocated calorific values, especially in grids with multiple feeding points.

##### 4.4.1 Allowed deviation

When applying the flow-weighted calorific value to a grid it is important to ensure that no end users are at a constant advantage or disadvantage by receiving gas with a significantly higher or lower calorific value than the calorific value allocated to the grid. Of special interest is to protect end users close to the feeding point with the lowest calorific value.

Both Germany and Denmark have introduced maximal limit for how much the flow-weighted calorific value is allowed to deviate from incoming calorific values, the so called “2% limit”. This limit means that the flow-weighted calorific value may be used for debiting provided that it does not deviate with more than  $\pm 2\%$  from the average calorific value for the settlement period of any of the incoming feeding points (Germany [43]) or lowest average incoming calorific value for the settlement period on a yearly basis (Denmark [42]).

The German “2% limit” is based on what demands historically have been placed on measuring equipment. In Denmark, the limit is based on calculations of different gas mixing scenarios of Danish and German gas [42,54]. However, these calculations do not take measurement uncertainty on site into account.

**Example 3:** Control of 2% limit (Germany) [43]

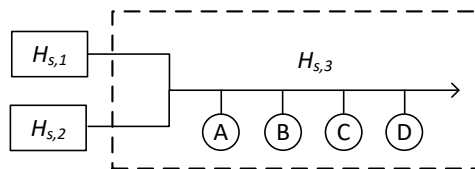


Figure 14. Gas grid with two feeding points and one calorific value zone

The flow-weighted calorific value  $H_{s,3}$  has been calculated according to Example 1 (Section 4.3.2). Next, a control is carried out to determine if the calculated calorific value deviated more than  $\pm 2\%$  from incoming average calorific values.

$$\frac{H_{s,3} - H_{s,1}}{H_{s,3}} \cdot 100 \leq \pm 2 \%$$

$$\frac{H_{s,3} - H_{s,2}}{H_{s,3}} \cdot 100 \leq \pm 2 \%$$

**Example 4:** Control of 2% limit (Denmark) [42]

The flow-weighted calorific value  $H_{s,3}$  has been calculated according to Example 1 (Section 4.3.2). Next, a control is carried out to determine if the calculated calorific value deviated more than 2% from the lowest incoming monthly average calorific value.

$$\frac{H_{s,3} - H_{s,low}}{H_{s,low}} \cdot 100 \leq 2 \%$$

If the difference exceeds 2%, a spread  $s$  is calculated based on the daily average calorific values that were used when calculating the monthly average. If  $s$  is less than 2% a correction is made to the lowest incoming average calorific value with a maximum of  $(2 - s)\%$  and the new corrected calorific value is used for debiting. If  $s$  instead exceeds 2% the lowest incoming average calorific value is used for debiting.

#### 4.4.2 Validation

Among the reviewed national regulations, only the Danish regulation thoroughly describe a process for regular validation of calorific values used for debiting [42]. In Denmark an annual control of the allocated calorific values is carried out by the Danish organization DGC. The validation process is the same regardless of type of end users or size of gas volume flows but differs between single feeding point and multiple feeding point grids. For grids with a single feeding point the control is carried out for, in the specific grid, a representative group of end users and the error is calculated on an energy basis. For grids with multiple feeding points the Danish "2% limit" (Section 4.4.1) is used and the control is carried out for all feeding points.

DGC performs all controls of the gas quality of Danish gas grid. Energinet.dk delivers daily and monthly average calorific values for all M/R stations in the transmission grid, while various distribution grid owners delivers the same information for all feeding points for the respective grid. Data has to be delivered to DGC at latest 10 working days after the turn of the month and DGC report their control results to the various net owners 20 working days after the end of the settlement period that is under revision. If the measured calorific values falls outside the accepted accuracy limit, the control frequency is increased from annual to monthly basis. In the case that the error persists over a period of six months, the grid owner is obliged to develop an action plan to resolve the error.

#### 4.4.3 Compensation due to incorrect debiting

There are no specific guidelines presented in the reviewed material for how to handle situations where incorrect debiting has occurred. The Danish regulations concerning the "2% limit" (Section 4.4.1) prevents that end users are debited for a higher calorific value than they have received [42]. Nothing is however mention regarding incorrect debiting due to systematic errors in measurements or the use of substitute calorific values. The German national regulations addresses incorrect debiting in conjunction with the use of substitute calorific values but only establishes that a correction should be made to the invoice based on the correct calorific value [43].

## 5 Discussion

There are many aspects to consider when developing a national regulatory framework for gas grids with multiple feeding points. The ensuing variations in gas quality does raise questions regarding equipment performance, calorific value allocation, quality control, debiting and responsibility. This report has presented earlier research on the topic together with how the issue is being dealt with in selected European countries (Denmark, Germany, Netherlands). Several important issues have been identified for how to move forward with the issue of varying gas sources and qualities in the Swedish system.

### 5.1 LESSONS FROM THE LITERATURE

Understanding how to efficiently operate gas grids is an important topic in the research literature since some time. Recently issues regarding the relation between use of gas, power, and heat have become more important as the dependency on intermittent renewable energy sources has increased. Advanced methods have been developed for how to analyze and optimize the operation of gas grids, but less attention has been given to issues of gas quality variations, maybe because this has not yet become an important issue in regions with the highest demand for natural gas.

### 5.2 DEALING WITH GAS QUALITY VARIATIONS

Using propanation of gases to balance the gas quality has several drawbacks, which are inevitable. It is directly a barrier for introducing more renewable energy, e.g. biogas, as the currently available propane is fossil, and is an indirect barrier as it adds to the cost for producers of renewable gases. It is also only a consistent way of handling gas quality variations as it relies on the largest incoming flow of gas to have a reliable quality, an assumption that in itself is being challenged.

Calculating flow-weighted calorific values is a well-documented and used method, but has its limitations in terms of acceptable variations and errors. Variations here relate to the actually allowed changes in the quality that is being transmitted, which may be set by technical specifications, and errors relate to the difference between measured values and calculated ones. In an increasingly complex grid with many gas sources, risks will become higher that both variations and errors increase beyond acceptable limits.

Quality tracking tools are advanced calculation tools that allows for the system in its entirety to be simulated and the quality to be determined by the simulations. Acceptable errors and variations must be determined also in the case of implementing a QT system, but this type of tool allows for higher precision and thus reduced risk of unacceptable errors. Although QT systems have been implemented and used for some time, they are still seemingly not well regulated. As the operation of a QT system will require resources it remains to be determined at which levels and grids this type of system should be implemented in, and how to share the costs.

### 5.3 OPTIONS FOR SWEDEN

The implementation of QT may be an interesting course of action, but the current lack of regulations surrounding it is of concern depending on implementation date. Especially the question of how to validate and preform periodic controls is of essence.

Whether the “2% limit” used in Denmark and Germany can be considered a reasonable limit for the Swedish system has to be evaluated based on the demands placed on measuring equipment in Sweden. An estimation or sensitivity analysis of what gas qualities can be expected has to be performed before a limit is set. This survey must take grid configurations into consideration.

The workgroup suggests that error propagation should be taken into consideration when deciding upon what limit should be set as the allowed deviation between measured and true calorific value in Sweden. By using measured calorific value data and error specifications of measuring equipment that is currently in use it is possible to assess what error can be expected in the process of calorific value allocation. Error propagation only accounts for the errors generated during measurement and conversion, not errors connected to varying gas quality.

Guidelines for validation and supervision of the calorific value in the Swedish gas grid should jointly be developed by the actors of the Swedish gas industry when a clear view of what different types of gas grids will be of interest is obtained. A suggestion is to follow the Danish model and assign a third party the responsibility of validation and supervision. One third party that could be of interest to involve is the Swedish national accreditation body SWEDAC.



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# MEASURING AND ENSURING THE GAS QUALITY OF THE SWEDISH GAS GRID

With the advent of more renewable gas in the Swedish natural gas grid, there is also more variations in quality expected. This renewable gas can stem from several sources, for example methane from anaerobic digestion and via thermochemical conversion of lignocellulosic material or indeed hydrogen from intermittent production of wind and solar power.

These gases have different properties than the gas on the grid and it is important to ensure that the measuring and assessment of the gas quality, and thus the debiting of the customers, is performed correctly.

This report uses other European countries national standards as examples on how this problem has previously been solved and discuss the implication of variations of gas quality on the Swedish natural gas grid.

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# Paper II





# Industrially integrated gasifiers for biochemical and biofuel production: A meta-analysis

Laura Malek\*, Per Tunå, Christian Hulteberg

\*Corresponding author: Email: [laura.malek@chemeng.lth.se](mailto:laura.malek@chemeng.lth.se)

Department of Chemical Engineering, Lund University, P.O Box 124, SE-221 00 Lund, Sweden

## 1 Introduction

The past decade has seen a substantial increase in the interest of a shift towards renewable energy and a biobased economy in the industrial sector [1]. The drivers behind this shift are the need to reduce the environmental impact of industries by reducing their dependence on fossil fuels and minimizing waste streams by process improvements or better utilization of low-value by-products. This shift has partly been the result of national policies, however, industries themselves strive towards more sustainable processes and optimizations that lead to higher profitability. One example of this is the increasing interest in integrating biomass gasifiers into existing industrial plants to produce biochemicals and/or biofuels, which can be used to replace fossil fuels in the plant, or sold to increase revenue.

A large number of techno-economic studies have been published in this field (e.g. [2–5]). The attractiveness of industrially integrated gasifiers for biochemical and biofuel production, compared to stand-alone gasification plants, lies largely in the synergistic effects that can be obtained between the gasification plant and the host plant. Integrating biochemical or biofuel production processes into the forest industry, for example, at sawmills, or pulp and paper mills, affords considerable advantages in feedstock handling, logistics and heat integration, compared to stand-alone gasification plants. In chemical pulp and paper mills black liquor can be gasified to produce syngas, instead of using a traditional recovery boiler (used for cooking chemical recovery), or the bark boiler could be replaced with a biomass gasifier. It is also possible to increase



the volume of syngas produced by including a solid-fuel gasifier in addition to a black liquor gasifier. This may lead to economies of scale in the downstream processing equipment required to upgrade the syngas and for chemical or fuel synthesis. However, Pettersson et al. have reported that this type of system expansion entails a substantial increase in biomass input, in some cases, more than double the intake of the original plant [6]. This will naturally affect the requirements of biomass handling.

Other host industries that can be of interest are process industries with a demand for steam or hot water, such as biomass-based combined heat and power (CHP) plants where, as in the case of the forest industry, synergistic effects can be obtained in biomass handling and logistics. There are several opportunities for integrating biomass gasification into existing industries, which is reflected in the diversity of the techno-economic studies available on the subject. It should be pointed out that although the same system setup has been considered (e.g. same gasifier and produced fuel), the results presented in different publications may differ significantly. Other researches has shown that the cost of producing, for example, SNG via indirect gasification varies from €0.05 to 0.21 [8–10]. System efficiencies also vary; for example, efficiencies in the range 45% to 56% have been reported in methanol production using entrained flow gasification [11,12]. These variations may be due to the use of different methods of calculating the system efficiency [13], variations in the definition of system boundaries, or variations in the technical and economic assumptions employed.

Publications often contain little or no information on specific calculation methods, system boundaries, assumptions, etc. One example of the way in which a lack of description of the calculation method can create discrepancies in the integration of biomass gasification into existing plants is the way in which the changes caused in the original operation of the industry are accounted for. When an industrial plant not only requires electrical power, but also produces it, a change in the demand/production in the integrated case can be accounted for as a change in the power demand or in the power export. Similar problems arise in economic calculations. As the year of publication can vary significantly between different studies, variations in monetary exchange rates must be taken into account.

These variations make it very difficult, and sometimes impossible, to make reliable comparisons of the technical or economic results. In theory, meaningful comparisons can only be made between different cases within a single study, and not between different studies. In order to make meaningful techno-economic comparisons between studies, it is necessary for different technologies and products to be evaluated on the same basis in terms of plant capacity, the energy content of the fuel produced, the cost of feedstock, method of calculating capital cost, the system boundaries, and the year in which the analysis was performed, etc.

The objective of this study was to survey the literature in the field of industrially integrated biomass gasification processes for biochemical and/or biofuel production, and to use the compiled data to draw conclusions on:

- what industries are seen as suitable for integration?
- which are the major end-products considered?
- in which region(s) is this a relevant research area?
- what, if any are the advantages to integrating biofuel production with a host industry?
- what are the economic gains to such an integration?

To this end, a comprehensive review of system studies was carried out, covering the type of host industries, the gasification technology used, the chemicals/fuels produced, system efficiencies, and economics. The main focus was on comparing system efficiencies, both as presented in the original publications, and recalculated on an equal basis. The recalculation was performed to be able to compare different studies on a fair basis for the first time and to allow visualization of potential trends over time. Another objective was to track the technical and economic data used in the reviewed publications to try to determine the extent to which original data were used, compared with existing data from other publications, when performing the studies. The results obtained from data tracking are presented graphically to provide a better overview of the connections between the studies and their reference material, especially the sources cited. In addition, the techno-economy has been investigated and results from several studies are presented on an equal basis, i.e. using the same input parameters for feedstock, energy and investment, allowing reliable comparisons to be made between different pieces of work and between different technologies.

This meta-study is a continuation and significant expansion of the work previously performed by Andersson et al. [13].

## 2 Methods and demarcations

This article has been divided into two parts. First part is a literature review, and the second a meta-analysis of the system efficiencies and economy presented in material obtained in the review. This section presents the methods used for compiling and analyzing the data.

## 2.1 Literature review

An extensive literature search was carried out in order to collect material in the form of publications (scientific papers and reports) relevant for this meta-study. The literature search was performed in June 2016, and Engineering Village was used as the search database. The terms used for the search were: biomass, gasification, integration. No restriction was put on the publication date of the articles. Additional material was provided by researchers at Chalmers University of Technology, Linköping University, Lund University and Luleå University of Technology. For a publication to be considered it had to be published in either the English or Swedish language, in addition to fulfilling all the following criteria:

- Biomass used as feedstock
- Thermochemical conversion technology using entrained flow, a fluidized bed or indirect gasifiers
- Motor biofuel or biochemical production
- Industrially integrated gasification plant

The criterion used in this study for a gasification process to be considered industrially integrated was feedstock and/or energy integration. Also, a two-way exchange of feedstock or energy between the added gasification plant and the host industry was required. A gasification plant only fed feedstock from the host plant without giving any form of material or energy back was not considered to be integrated, but a stand-alone gasification plant. The definitions of feedstock integration and energy integration are [14]:

- Feedstock integration: utilization of existing internal material streams that can be used in conversion processes (bark, black liquor and other industrial by-products)
- Energy integration: the exchange of energy flows between gasification plant and the existing industrial plant

Only publications giving mass and energy balances were included in this study as these are required for the comparison of system efficiencies on an equal basis. To limit the amount of material, patents and publications concerning the energy sector were excluded. For this reason, no studies on dedicated district heating plants or CHP systems were reviewed.

### 2.1.1 Data handling

The findings in the publications included in this meta-study were either based on original data or existing data from previous studies. For example, a plant configuration established in a previous study can be used in a later study, but with different material balances. To determine the extent to which original technical and economic data were used, compared with pre-existing data, the data used in the publications were tracked by noting the references made to existing studies when referring to technical and economic parameters. The visualization and exploration software Gephi [15] was used to review the results for studies using data from previous studies. This was done by performing an adjacency study using all relevant references, excluding original data and personal communications. The reason for this exclusion was to track only source material that had been published. References to technical and economic data were analysed separately, to visualize connections between the studies and their reference material.

## 2.2 Meta-analysis

Meta-analysis was divided into two parts, where the first part in detail examines the system efficiencies presented in the reviewed material, whereas the second part presents economic recalculations for better comparing economic performance between different studies.

### 2.2.1 Meta-analysis of system efficiencies

As mentioned above, it is difficult to compare the efficiency of different gasification systems due to variations in system boundaries and system efficiency calculation methods. In order to be able to make reliable comparisons of the findings given in different studies it is necessary to re-evaluate the results and energy balances on an equal basis. The method of electricity equivalents was used for all energy carriers in this study. A system that converts low exergy into high exergy with good efficiency will receive a higher electricity equivalent efficiency than traditional system efficiency. For example, a system that uses only biomass as input will have a higher electricity equivalent efficiency than traditional system efficiency, compared to a system using both biomass and electrical power as input.

All mass end energy balances were *reported on an incremental basis*, compared to the stand-alone operation of the plant prior to integration, i.e., the required marginal supply of biomass and other energy carriers needed to produce a motor fuel or chemical. The system efficiencies were calculated using Eq. 1 for traditional system efficiencies (SE), and Eq. 2 for system efficiencies based on electricity equivalents (EE), as described

by Tunå et al. [16]. The values of efficiency used for conversion to electricity equivalents are presented in Table 1.

$$SE = \frac{\sum Q_{output}}{\sum Q_{input}} \quad \text{Eq. 1}$$

$$EE = \frac{\sum \eta_{output} \cdot Q_{output}}{\sum \eta_{input} \cdot Q_{input}} \quad \text{Eq. 2}$$

**Table 1. Power generation efficiencies used for the calculation of electricity equivalents. LP – low-pressure; MP – medium-pressure; IP – intermediate-pressure; HP – high-pressure**

Fuel	$\eta$	Reference
Biomass	46.2%	[17]
District heating	10.0%	[16]
Liquid fuels	55.9%	[16]
SNG	57.6%	[18]
H2	58.3%	[18]
LP steam, 4.5 bar(a) 150°C	16.6%	[19]
MP Steam, 11 bar(a) 200°C	19.6%	[19]
IP Steam, 26 bar(a) 275°C	22.6%	[19]
HP steam, 81 bar(a) 490°C	27.2%	[19]

Liquid fuels covers DME, FT-fuels and MeOH. Additional liquid fuels such as petrol and EtOH are also assumed to have an electricity efficiency of 55.9% as no values were found in literature. The electricity efficiency of gaseous fuels such as natural gas was similarly assumed to be the same as for SNG, i.e. 57.6%.

When using incremental mass balances, changes in the original operation must be properly accounted for. For example, there are cases in which electricity is exported in both the host plant and the integrated case, however, the export is lower in the integrated case than in the base case. On an incremental basis, this difference can either be regarded as a reduction in export, i.e. a negative output, or as an increase in power demand, i.e. a positive input. The same reasoning can be applied to reduced system inputs. In this study a loss in export compared to the operation of the base case was considered to be a system input, while a saving in input was considered to be a gain, and thus regarded as an output. This was done to avoid negative values in the energy balances.

## 2.2.2 Meta-analysis of process economics

Economic recalculations were performed to enable comparisons of investment and operating costs between studies published in different years. The investment costs were updated to values in 2016 using the Chemical Engineering Plant Cost Index (CEPCI) [20]. It is, however, important to note that it is not recommended that the CEPCI be used over a period exceeding five years, as the uncertainty in the predicted values can exceed the inherent uncertainty in budgetary cost estimates. The CEPCI was used here for economic recalculations for all the studies, despite the fact that some of the studies included were more than five years old. This will lead to a higher uncertainty in the results, but will still give an indication of current prices.

# 3 Literature review summary

The 35 publications included in this meta-study are presented below. Table 2 gives a list of the reviewed publications, together with information on feedstock, the main product, and type of gasification technology used. All the publications reviewed included at least one case on motor fuel or chemical production by industrially integrated biomass gasification, resulting in a total of 138 cases. However, only the cases/scenarios that met the criteria given above are listed in Table 2 and the reviewed articles may contain additional cases describing, for example, stand-alone gasifiers. The gasifier technologies were divided into entrained flow, fluidized bed and indirect gasification. The studies in the reviewed articles has either been carried out on existing plants (E), or hypothetical plants (H), which are generic or based on model simulations. Special note is made for hypothetical plants that are based on a known model (The Ecocyclic Pulp Mill, KAM [20], KAM2 [21], FRAM [22]).

**Table 2. List of reviewed publications. EF – entrained-flow; FB – fluidized-bed; I – indirect gasification**

Ref.	Feedstock	Product(s)	Gasifier	E/H
[23]	Black liquor	H <sub>2</sub>	EF	H*
[24]	Black liquor	H <sub>2</sub>	EF	H*
[11]	Bark, black liquor and wood chips	MeOH	EF	E
[25]	Bark and wood chips	Ammonia	EF	E
[26]	Black liquor and pyrolysis oil	MeOH	EF	E
[27]	Biomass (unspecified)	SNG	I	E
[28]	Forest residues	H <sub>2</sub>	I	E
[29]	Black liquor and biomass residues	DME, FT, MA	EF, FB	H

**Table 3. List of reviewed publications - Continuation**

[3]	Black liquor	DME, FT, MeOH	EF	H*
[30]	Black liquor	DME, EtOH	EF	H#
[31]	Biomass (unspecified)	MeOH	FB	E
[32]	Biomass residues	FT	I	H
[33]	Bark, forest and sawmill residues	FT, MeOH	FB	E
[34]	Forest residues	FT	EF	E
[35]	Black liquor	DME	EF	H+
[36]	Bark, wood chips and waste wood	H <sub>2</sub>	DB, FB, EF	E
[37]	Switchgrass residues	FT, H <sub>2</sub> , SNG	FB	H
[38]	Wood chips	MeOH	FB	E
[39]	Jatropha seed husk	H <sub>2</sub> , MeOH	I	H
[40]	Biomass residues	FT	FB	H
[41]	Sawmill residues	SNG	FB	H
[42]	Black liquor	DME, SNG	EF	H+
[43]	Black liquor and dry black liquor	MeOH	EF, FB	H+
[44]	Dry black liquor	H <sub>2</sub>	FB	H+
[45]	Dry black liquor	SNG	FB	H+
[46]	Dry black liquor	SNG	FB	H+
[47]	Black liquor	DME	EF	H*
[6]	Black liquor	DME, FT, MeOH	EF	H#
[48]	Bark and black liquor	DME	EF, FB	H
[49]	Bark	SNG	FB	E
[50]	Bark and biomass (unspecified)	DME, FT, MeOH	EF, FB, I	H+
[51]	Sugarcane bagasse	FTD, FTG	FB	H
[52]	Black liquor	DME	EF	H
[53]	Bark and forest residues	DME	FB	E
[54]	Bark, logging and fiber residues	SNG	I	E

The studies were published during a period spanning eleven years; the earliest being that by Ekbohm et al. [3], published in 2005, and the most recent that by Holmgren et al. [31] in 2016. The majority of host plants were chemical pulp and paper mills (24), while bioethanol plants, chemical plants, mechanical pulp and paper mills and oil refineries were the host plants in two studies each. A biodiesel plant, a sawmill and a steel plant were the host plant in one study each.

It was noted that the majority of the reviewed publications originated from Sweden, and were based on studies of Swedish or Scandinavian plants. Most of the studies in other countries found during the literature search concerned stand-alone biomass gasification for motor fuel production, rather than integrated biomass gasifiers. This may imply that there is a current lack of interest in industrially integrated biomass gasifiers in other countries.

Several additional studies on industrially integrated biomass gasifiers identified in the literature search were rejected as they did not fulfil the selection criteria. The most common reason for studies being rejected were a lack of two-way exchange of feedstock/energy between the added gasification plant and the host industry ([55–59]), and a lack of mass and energy balances ([60–62]).

### 3.1 Host industry

The distribution of host plants according to type, and the number of existing plants and hypothetical plants studied can be seen in Table 3.

**Table 4. Type of host plant and number of existing an hypothetical plants studied**

Host plant	Number of studies		
	Existing	Hypothetical	Total
Biodiesel plant	-	1	1
Bioethanol plant	-	2	2
Chemical plant	2	-	2
Chemical pulp and paper mill	6	18	24
Mechanical pulp and paper mill	2	-	2
Oil refinery	2	-	2
Sawmill	-	1	1
Steel plant	1	-	1

There are several possible reasons for the high representation of chemical pulp and paper plants in the studies performed. The main factor that makes chemical pulp and paper mills so attractive is the presence of black liquor. Modern chemical pulp mills produce 1.7-1.8 tonnes of black liquor (dry content) per tonne of pulp produced [3]. Based on conventional pulp mill sizes, this translates into a potential energy source of 250-500 MW per mill, and as modern chemical pulp mills produce a net surplus of energy, this alternative is attractive for the conversion of black liquor into high-value energy carriers. Bearing in mind the increase in energy prices and greater competition for raw materials, this would provide an opportunity for extra revenue in the pulp and



paper industry [63]. It should also be pointed out that it was concluded in many of the studies reviewed that integrating a biomass gasifier for motor fuel production in a pulp and paper mill would indeed constitute an attractive investment opportunity (e.g. [3,5,48,64]).

Surprisingly, mechanical pulp and paper mills and sawmills occurred in only a few studies, despite being part of the forest-based industry. Isaksson et al. studied cases where a sawmill is co-located with a mechanical pulp and paper mill [33]. However, although the sawmill provides bark for the gasifier, in addition to pulp chips for the mechanical pulp and paper mill, the gasifier is integrated with the pulp and paper mill, and is therefore not included in the sawmill category. One explanation of the low representation of other types of host plants could be that, unlike plants in the forest-based industry, the on-site availability of biomass suitable for gasification is lower, leading to lower profitability. Although biomass is handled at biodiesel [39] and bioethanol [37,51] plants, the fraction of biomass that would be suitable for gasification is significantly smaller, and often of a much lower quality than the fraction used for the main product. Another explanation could be that the residual biomass fraction is used for other purposes, which would create competition for the feedstock. For example, Walter & Ensinas studied the use of bagasse from an ethanol production plant as feedstock for the gasifier [51]. However, bagasse is also often burnt for heat and power production within ethanol plants, or used as a wood substitute, for example, for the production of pulp and paper products.

There are also opportunities for integration in industries that are traditionally not associated with biomass processing, such as oil refineries and steel plants. Oil refineries are of interest due to the existing downstream processes associated with fuel production (distillation, cracking, gas cleaning, etc.). Excess off-gases generated in the steel making process can be processed together with syngas from biomass gasification to obtain various types of products [65].

## 3.2 Gasifier capacity

The reviewed publications included cases where entrained flow, fluidized bed or indirect gasification technology and there is a wide range in the capacity of the integrated gasifiers considered. Figure 1 shows the range in thermal input capacity and average thermal capacity (both based on the lower heating value, LHV), for the different gasification technologies found in the publications reviewed. Most studies present the gasifier capacity based on a LHV basis, however, some cases occur where the authors have stated the use of the higher heating value (HHV). These values were

recalculated based on the LHV using Eq. 3, where H denotes the heating value and  $w$  the mass fraction.

$$H_{LHV} = H_{HHV} - \Delta H_{vap,H_2O}^{298K} (8,94 \cdot w_{hydrogen} + w_{water}) \quad \text{Eq. 3}$$

In studies where this was not specified, it was assumed that the LHV had been used. Pettersson & Harvey, did not specify the gasifier capacities [66], but these were obtained from the authors. No information could be found on the gasifier capacity in one study [35].

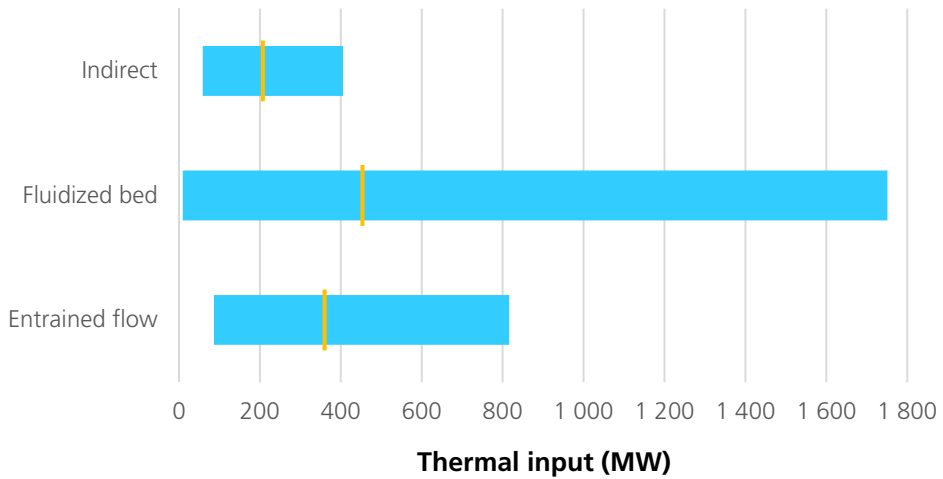


Figure 1. Range in thermal input capacity of the different types of gasifiers. The average gasification capacity is indicated by the green line.

All three gasification technologies are generally considered to be capable of high production capacities. However, the capacity of fluidized bed and entrained flow gasifiers is currently much greater than that of indirect gasifiers, and these technologies are thus considered to be the most suitable for large-scale biomass gasification [67,68]. Ranges in the capacity of the different technologies vary in the literature, but typical values are: indirect gasification 5-20 MW, fluidized bed gasification 10-100 MW and entrained flow gasification 50-1,000 MW [67–69].

Indirect gasifiers are usually not pressurized, which is problematic when scaling up the reactors, and explains why their capacity is limited to < 50 MW per gasifier. Several gasifiers are therefore required to achieve greater capacity. This is not specific to indirect gasifiers, as most reactors are limited by their physical size. The advantage of indirect gasifiers is the low level of nitrogen, removing the need for oxygen as an oxidizing agent,

making these gasifiers suitable for low-cost syngas production. The disadvantage of reactors at near atmospheric pressure is that larger equipment is required, which increases the cost of syngas compression prior to motor fuel or chemical synthesis.

Entrained flow gasifiers generally have the highest gasification capacities, but as can be seen in Figure 1, the fluidized bed gasifiers had greater capacities in the reviewed publications. Some of the largest thermal capacities were found in the study by Pettersson et al., where fluidized bed gasifiers with capacities up to 1,750 MW were considered [48]. The overall lowest gasification capacity was also found among the fluidized bed gasifiers, in the study by Mesfun et al. on the integration of a 9.4 MW fluidized bed gasifier in a sawmill [41]. The average value for fluidized bed gasifiers given in Figure 2 is about 450 MW. However, this is the a result of the extremely large gasification capacities in the study by Pettersson et al. [48]. In 24 out of 55 cases the capacity of fluidized bed gasifiers was in the range 200-300 MW (e.g. [15,37]), which is higher than the values given in the literature.

All the cases involving entrained flow gasifiers were within the capacity range found in the literature; the lowest capacity being a 86.4 MW biomass gasifier [36] and the highest a 816 MW biomass gasifier [11]. The average thermal capacity of the gasifiers included in this study was smaller for entrained flow gasifiers (360 MW) than for fluidized bed gasifiers. This is because half of the fluidized bed gasifiers had a capacity in the ranges 200-250 MW (e.g. [15,34,42]) or 300-350 MW (e.g. [6,29]), and most of the remaining studies involved black liquor gasification at capacities just below 500 MW (e.g. [3,48]).

As in the case of fluidized bed gasifiers, the capacity of the indirect gasifiers extended beyond what is currently considered realistic for a single unit. Brau et al. studied the integration of the largest indirect gasifier (406 MW) in an oil refinery [28], while the lowest capacity (58.7 MW) was found in a study on a biorefinery based on jatropha seed husks by Martinez-Hernandez et al. [39]. (Both these capacities were recalculated from the HHV to the LHV basis according to Eq. 3.) The indirect gasifiers had the lowest average gasification capacity in the studies considered (207 MW), and the capacity was between 200 and 230 MW in over half the cases.

The studies by Andersson et al. [11] and Pettersson et al. [48] are two examples of studies in which very large gasification capacities (816-1,750 MW) were found to be necessary in certain scenarios. Whereas capacities up to 1000 MW are possible with single entrained flow gasifiers, fluidized beds tend to have a capacity limit around 100 MW. It is therefore important to note that the values presented in most of the publications reviewed refer to the total installed gasification capacity, and not the capacity of an individual gasification unit, as industries requiring a high capacity would

install a train of smaller gasification units, rather than one large unit. However, many of the studies have been performed from a holistic viewpoint, and there is often no technical information on how the gasification island is configured. The technical feasibility of gasification capacities has thus generally not been discussed in the reviewed publications.

Each gasification technology has its own technical advantages and limitations, which must be taken into consideration when choosing the appropriate technology. The choice is largely dependent on process aspects such as feed characteristics, the desired end product and the production scale. Fluidized bed gasifiers (including indirect gasifiers) are very tolerable to variations in feed particle size, which makes them suitable for a wide range of biomass types [69]. Also, these gasifiers can be operated under atmospheric pressure or pressurized conditions using various fluidization media. One disadvantage of fluidized bed gasifiers compared, for example, to entrained flow gasifiers, is that the particle content in the outgoing gas is high due to the small particle size of the bed material and fuel particles. This technology is, however, considered flexible, and this has contributed to fluidized bed gasification becoming well established globally for heat and power applications.

Entrained flow gasification systems are more complex than fluidized bed systems, and higher capacities (often over 200-250 MW) are therefore required to achieve economies of scale. Entrained flow gasifiers are considered less flexible as they require a pressurized environment, pure oxygen as oxidizing agent and small biomass particle sizes or a liquid/slurry feed to maintain stable operation. These feed requirements make black liquor a suitable feedstock for entrained flow gasifiers, whereas solid biomass fuels place high demands on pretreatment and the fuel feeding system. On the other hand, less strain is placed on the subsequent gas cleaning process due to the relatively tar-free gas produced by entrained flow gasification.

### 3.3 Fuels

Tables 4 and 5 present a summary of the number of cases found considering biofuel production in the different industries, and using the different gasification technologies, respectively. The total number of cases in each of the tables exceeds 138 (the total number of cases in the reviewed publications) as some of the cases produced more than one type of fuel, or more than one type of gasifier was used to produce a particular fuel. For example, in one of the cases in the study by Consonni et al., an entrained flow and a fluidized bed gasifier were used simultaneously to produce mixed alcohols [29].

**Table 5. Number of cases found for the different industries**

Host plant	Product							
	DME	EtOH	FT	H <sub>2</sub>	MA	MeOH	NH <sub>3</sub>	SNG
Biodiesel plant	-	-	-	1	-	1	-	-
Bioethanol plant	-	-	6	1	-	-	-	2
Chemical plant	-	-	-	-	-	2	-	3
Chemical pulp and paper mill	51	1	26	4	1	15	1	5
Mechanical pulp and paper mill	-	-	2	-	-	2	-	1
Oil refinery	-	-	-	8	-	-	-	-
Sawmill	-	-	-	-	-	-	-	7
Steel plant	-	-	-	-	-	2	-	-

**Table 6. Number of cases found using the different gasification technologies**

Product	Gasification technology		
	Entrained-flow	Fluidized-bed	Indirect
DME	35	20	2
EtOH	1	-	-
FT	19	12	3
H <sub>2</sub>	5	3	6
MA	1	1	-
MeOH	11	9	3
NH <sub>3</sub>	1	-	-
SNG	2	12	4

As can be seen from Tables 4 and 5, chemical pulp and paper mills and entrained flow technology are overrepresented. This was to be expected as the majority of the publications reviewed involved chemical pulp and paper mills. DME was found to be the most common fuel produced, followed by FT fuels. The popularity of DME is probably the result of most of the studies being performed on chemical pulp and paper mills, many of them using the technically proven CHEMREC technology, in which black liquor is gasified using entrained flow gasification to produce DME [70,71]. Fluidized bed technology is also very common, probably due to the gasification of bark generated at the pulp mill. FT fuels are also almost exclusively produced in the pulp and paper industry, mainly using entrained flow or fluidized bed gasification.

In oil refineries there is a clear advantage of producing hydrogen as it is required for hydrocracking and sulphur-removal processes. Another product that would have been

of interest is FT products due to existing downstream processes such as distillation and cracking. It is therefore surprising that no such cases were found.

Entrained flow technology is not suitable for producing SNG or methane due to the low methane content in the raw syngas (<1.5 mole%). Fluidized bed and indirect gasifiers, on the other hand, can produce syngas with methane contents in the range of 5-10 mole% and 10-15 mole%, respectively, and are therefore preferred as the final fuel product has a high concentration in the raw syngas. The large number of cases of SNG production at a sawmill is due to one particular study dealing with this specific topic [41].

### 3.4 Origins of the data

By tracking the references to technical and economic data in the reviewed publications it is possible to obtain an idea of the amount of original data used in each study, compared to existing data. Listing the citations also provides an overview of the connections between publications. Figure 2 shows the citation connections for the technical data in all 35 reviewed studies.

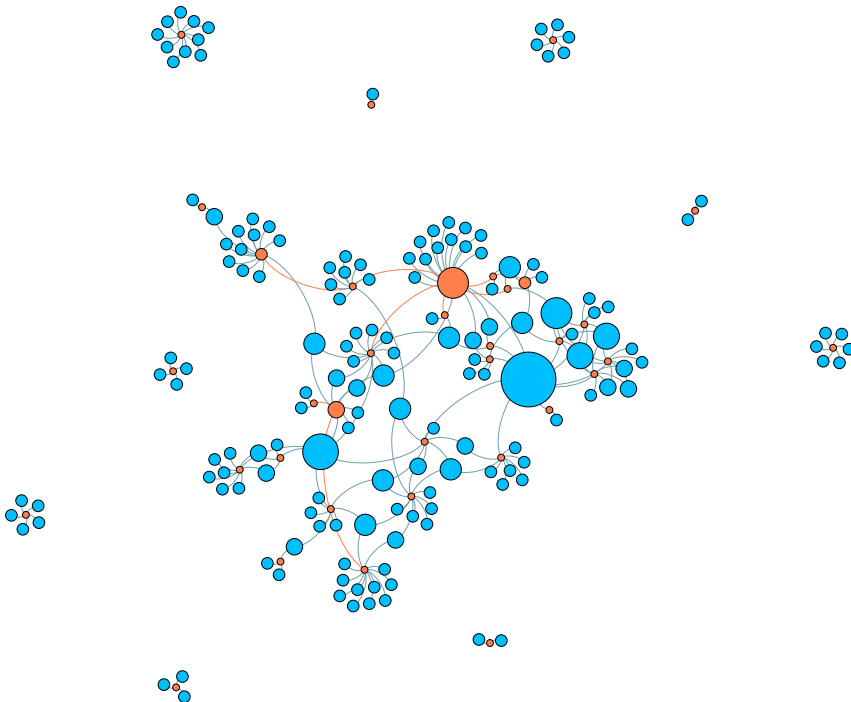


Figure 2 Connections between the citations to technical data in the reviewed publications. The orange symbols represent the reviewed publications, and the blue symbols the cited publications. The connections between them are shown by the grey lines. The size of the symbols represents the number of citations in the publication.

The number of citations to technical data in each study varies from one to sixteen, with an average of 6.3 citations per study. Data tracking shows that the majority of the references are only cited in one or two studies each, showing a wide spread in the data used in the different studies. However, some references have been cited in five or more of the publications. References to Ekblom et al. [3] and KAM [72] have been cited five times each, Hamelinck & Faaij [73] six times, and the most cited reference is to Ekblom et al. [64], with ten citations. The two publications by Ekblom et al. [3,64] are part of an EU/ALTENER project investigating the production of motor fuels from black liquor gasification, while the KAM report [72] is part of the Ecocyclic Pulp Mill Programme. Citations to Hamelinck & Faaij [73] refer to gas cleaning and upgrading operations. As most of the reviewed publications deal with black liquor gasification in chemical pulp and paper mills, most of the citations would be to papers and reports of the same type. However, this also indicates that the research is founded on a relatively narrow base. It is also important to note that although the paper by Hamelinck & Faaij [73] was published in a scientific journal, the two studies by Ekblom et al. [3,64] and the KAM report [72] were not published in peer-reviewed journals.

The majority of the reviewed publications and their citations are connected in a large cluster. There are, however, nine isolated islands where studies share no citations with any other studies: Ince et al. [32], Laser et al. [37], Lundgren et al. [38], Martinez-Hernandez et al. [39], McKeough & Kurkela [40], Mesfun et al. [41], Tunå et al. [15], Wetterlund et al. [53] and Zhang et al. [54]. The reasons for these islands vary. In some cases, the host industry only appears in that specific study (Laser et al. [37], Lundgren et al. [38], Martinez-Hernandez et al. [39], Mesfun et al. [41]), reducing the likelihood of shared citations. In the case of Ince et al. [32], although the study considered a chemical pulp and paper mill, it originates from the USA, unlike the majority of the studies which were Swedish. The same could apply to the study by McKeough & Kurkela [40], which originates from Finland, although the explanation probably lies in the fact that this publication only has one reference. Of the three remaining islands, Tunå et al. [15], Wetterlund et al. [53] and Zhang et al. [54], the first two studies considered chemical pulp and paper mills, while the third involves a mechanical pulp and paper mill, all located in Sweden. It is unclear why these three Swedish studies do not share any citations with any of the other studies reviewed. However, it is highly probable that at least some of the references are closely related to others in the large cluster. For example, Tunå et al. [15] and Pettersson et al. [6] use data from the FRAM project, but cite different references. Also, Wetterlund et al. [53], Andersson & Lundgren [25] and Andersson et al. [26] use original data from a BillerudKorsnäs AB mill.

As mentioned above, references to original data and personal communications were excluded from the data tracking analysis. Out of the 35 publications reviewed, 14 used original data to some extent [3,25,26,28,29,31,33,34,36,38,39,49,51,53].

A similar data tracking analysis was performed for the economy data cited in the reviewed publications. Out of the 35 publications studied, 18 included economic calculations (see Table 7). Figure 3 shows the citation connections for the economic data. References to original economic data were found in five of these studies [3,26,29,31,74] and these are not included in the figure.

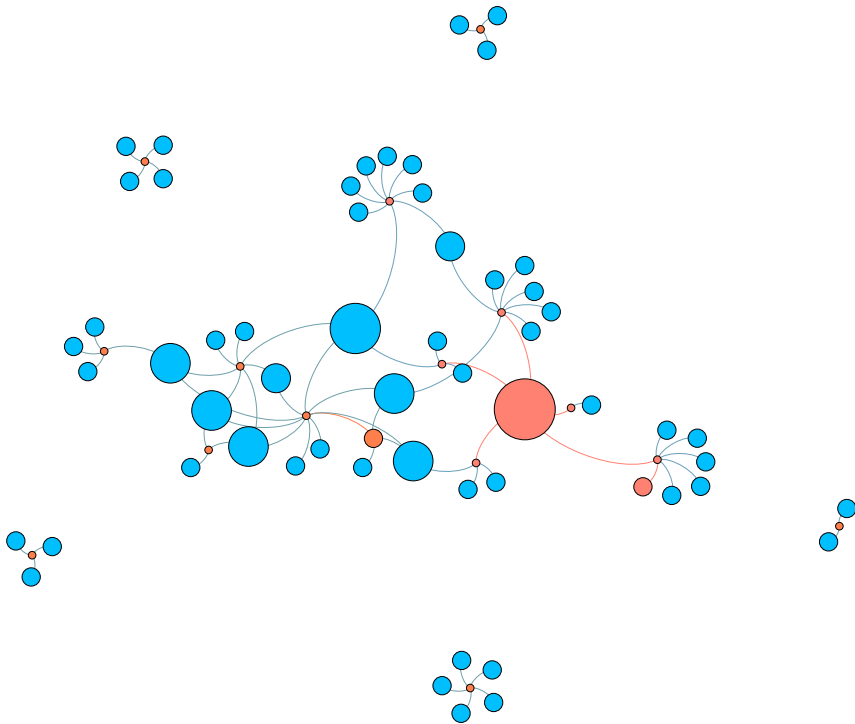


Figure 3. Connections between the citations to economic data in the reviewed publications. The orange symbols represent the reviewed publications, and the blue symbols the cited publications. The connections between them are shown by the grey lines. The size of the symbols represents the number of citations in the publication.

There is a slightly smaller variation in the number of citations to economic data in each study than in the technical data. The number of citations ranges from one to ten, with an average of 4.1 citations per study. Similar to the technical data, most references to economic data are only cited once. The most cited publications are Hamelinck & Faaij [73] with four citations, and Ekbohm et al. [3] with five. As in the case of citations to technical data, the higher frequency of citation of these references is probably due to



the fact that the majority of the reviewed publications deal with black liquor gasification in chemical pulp and paper mills.

Five isolated islands can be seen: Holmgren et al. [31], Ince et al. [32], Laser et al. [37], McKeough & Kurkela [40] and Zhang et al. [54]. Four of these five also formed islands in the technical data tracking analysis, and the reasons for this are likely to be the same, namely country of origin and type of host plant. In the case of Holmgren et al. [31], the island may be the result of the authors citing their own previous publications, where the economic parameters were described in more detail. Relevant references may be found in these previous publications.

### **3.4.1 The source of the data used in the most cited publications**

As seen in the previous section, some studies are cited more often, regarding both technical and economic data. Further data tracking was therefore performed for the most cited studies. In the case of technical data, the publications by Hamelinck & Faaij [73] and Ekbom et al. [64] were studied further. The study by Hamelinck & Faaij [73] is also frequently cited for its economic content, and was therefore subject to further economic data tracking together with the study by Ekbom et al. [3].

The study published by Hamelinck & Faaij [73] contains extensive and detailed tables covering both operational and economic parameters for various unit operations used in biomass gasification processes. Studies that have referenced this publication have stated which specific operational or economic data were used, and therefore only the sources concerning that data will be presented here. The unit operations for which data have been cited are gas cleaning equipment [75–77], reformers [78,79], shift reactors [78], synthesis reactors [78,80–84] and pressure swing adsorption systems [78]. Regarding economic data, citations refer to pre-treatment equipment [85,86], an oxygen plant [80], various gas cleaning equipment [77,85], compressors [77], shift reactors [87] and pressure swing adsorption systems [78]. In addition, the economic table includes overall installation factors [85] and maximum unit operation size [77]. Finally, a reference was made to the assumed operating costs (including maintenance) which itself has been taken from previously published work [85,88]. The year of publication of these references ranges from 1993 to 2000. In the case of technical data, process technology may remain relatively unchanged for several decades, and the use of process data that are more than 20 years old is considered acceptable. Economic data, on the other hand, are more sensitive. As mentioned above, recalculation of values and costs over a period exceeding five years is not recommended. This does not necessarily mean that the economic data presented by Hamelinck & Faaij [73], and the publications citing it, are erroneous or inaccurate. However, the reliability of the data can be questioned.

There is often a clear difference between academic publications and consultant reports regarding references to other studies and the data used; citations tending to be fewer in the latter. Hamelinck & Faaij [73] make very specific references to the source of data, while Ekbohm et al. [64] make more general references to companies and conversations, making it difficult to determine the exact source of the information. Citations made *to* Ekbohm et al. [64] in the reviewed publications can, however, mainly be divided into two categories: references to the host pulp and paper mill, and references to black liquor gasification and fuel synthesis. Ekbohm et al. [64] use reference mill data from several KAM project reports [20,21,89], while black liquor gasification is based on the [70,71]; both references being to conference proceedings. Additional citations are made in the reviewed publications regarding the causticizing process, but Ekbohm et al. [64] give no clear indication of the origin of this information. Also, Haldor Topsøe AB is mentioned throughout the report regarding the technology used for fuel synthesis, but no references are given to the company in the report. Considering the scarcity of references in this report, it can be assumed that much of the information is based on in-house data collected by the authors or through personal communications.

The studies carried out by Ekbohm et al. are presented in two reports, one concerning technical aspects [64] and the other economic aspects [3]. References to the slightly later study [3] are related to the costs of individual unit operations, overall capital cost, operating cost and pricing of utilities. The cost data presented in this study are based almost entirely on quotations from various companies. The costs of some of the units, for example, a steam turbine and the limekiln, are based on in-house estimates, probably made using base cost estimation procedures.

## 4 Meta-analysis results

In this section the results of the meta-analysis with respect to system efficiency and economic performance are presented on an equalized basis.

### 4.1 System efficiency calculation on equal basis

The electric equivalent recalculation method was also used to compare the conversion of biomass into biofuels or biochemicals on an equal basis, and is a measure of how much exergy has been preserved in the system. Figure 4 shows the relation between system efficiency (SE) and the system efficiency based on the electric equivalent (EE) method for 137 of the 138 cases in the reviewed publications. (One case (SNG) was excluded as the data point was far from the rest of the data, with an efficiency exceeding 200%.) The figure shows each of the main products (DME, FT, H<sub>2</sub>, MeOH and SNG)

as separate data sets. Cases in which the product only appears in one case (ammonia and mixed alcohols), and cases in which two different fuels are produced in the same case (DME/EtOH, FT/SNG) constitute a separate data set denoted “other”. The material balance was not given in the study by Tunå et al. [15], but was obtained from the authors.

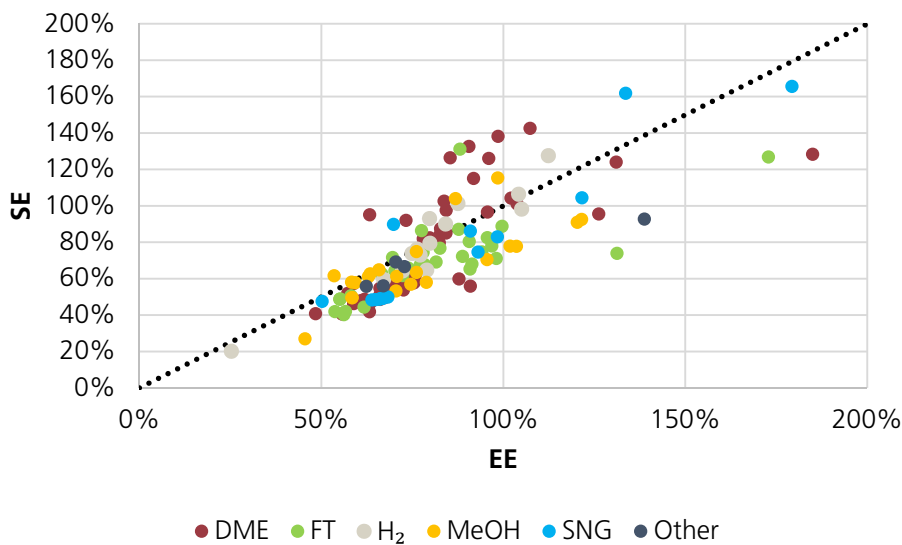


Figure 4. SE vs. EE. The dotted line is the line of equality, i.e. SE=EE.

In most of the systems studied, EE was higher than SE, meaning that these systems convert low exergy into high exergy with good efficiency. The recalculated system efficiencies range from 20%/25% (SE/EE), reported for H<sub>2</sub> production [39], to 347%/275% (SE/EE) for SNG production [42]. System efficiencies exceeding 100% are not uncommon when material balances are calculated on an incremental basis. This does not necessarily mean that the efficiency of the plant increases after integration, but is an effect of resources being used differently. This occurs when an internally available energy surplus in the form of either feedstock or energy streams from the base case is converted into biofuel in the integrated case, e.g. bark being gasified instead of exported. There are cases where the system efficiencies exceed 100% for all the main fuels.

It can be seen from Figure 4 that EE is generally higher than SE for FT, MeOH and SNG. In the cases of DME and H<sub>2</sub> the data points are more evenly distributed around the line of equality. The spread in the data around the line of equality is less for the H<sub>2</sub>

data, however, this could be due to the fact that there are relatively few data points for H<sub>2</sub>. No other patterns could be discerned in the data.

Cases showing a large deviation between SE and EE were subjected to more detailed analysis in an attempt to identify the cause of this deviation. This was done by breaking down the system efficiencies into product, power and steam in order to see the system efficiency share of each subgroup. Cases from all major fuel groups were selected, and the comparison between SE and EE is shown in Figure 5.

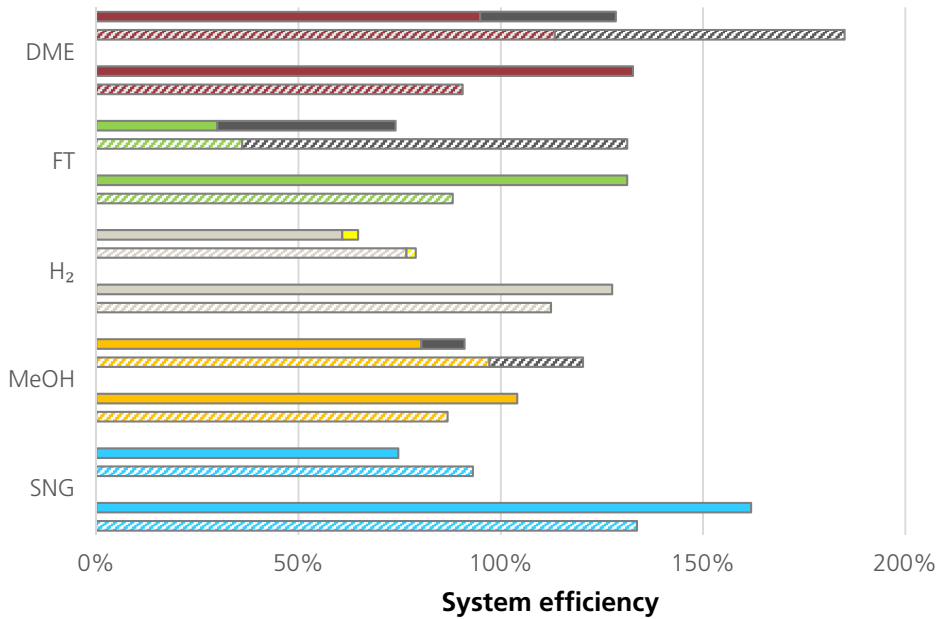


Figure 5. Comparison of SE and EE for cases showing a large deviation. The filled bars show SE and the hatched bars EE. Black and yellow bars represent electrical power and steam respectively.

For cases where power is an output, EE is higher than SE, which is a result of the electric equivalent method described above. The more power produced, the higher EE, as can be seen for the first FT case, where output power constitutes about 60% of the SE output, but almost 80% of the output on the EE basis. In the cases of H<sub>2</sub> and SNG, where there is no power output, the upper cases show a higher EE than SE, while the opposite is seen in the lower cases. The reason for this is that the proportion of input from power is higher than that from biomass in the lower cases.

## 4.2 Economy

The reviewed publications including economic calculations were analysed in further detail to investigate the different specifications, conditions and assumptions used in the calculation of investment and production costs. The incremental costs were taken from the publications so as to account only for the investments pertaining to biofuel and/or biochemical production. Based the information collected, the specific investment costs were recalculated on an equal basis together with the recalculated operating costs and other assumptions regarding investments. Of the 35 studies reviewed, 18 contained cost data. These are listed in Table 6 together with the industrial and economic specifications relevant for the comparison of investment and production costs.

**Table 7. Publications including economic data**

Ref	Industry	Interest rate (%)	Depreciation (years)	Operating time (h/y)
[24]	Chemical pulp & paper mill	5	20	8000
[11]	Chemical pulp & paper mill	10	20	8000
[25]	Chemical pulp & paper mill	10	20	8000
[26]	Chemical pulp mill	-	-	8352
[29]	Chemical pulp & paper mill	11.5	25	8330
[3]	Chemical pulp & paper mill	10.1	25	8330
[30]	Chemical pulp & paper mill	6	15	7838
[31]	Chemical plant	-	-	8000
[32]	Chemical pulp & paper mill	7.8	15	-
[35]	Chemical pulp & paper mill	6	25	-
[37]	Bioethanol plant	10	25	8400
[38]	Steel plant	7.6	20	8000
[40]	Chemical pulp & paper mill	10	20	-
[41]	Sawmill	4	20	8000
[47]	Chemical pulp & paper mill	-	20	8000
[50]	Chemical pulp & paper mill	7	10	8330
[53]	Chemical pulp & paper mill	-	-	8000
[54]	Mechanical pulp & paper mill	-	-	8000

The specific investment cost, i.e. the incremental investment cost per MW of main product produced, was calculated in the above cases. The production of hydrogen, ammonia and mixed alcohols, and cases where two different fuels are produced in the same plant (DME/EtOH, FT/SNG), were not included in this analysis as it would not be possible to see any trends in such small data sets. Figures 6 show the specific investment cost in €<sub>2016</sub> per MW product for DME, FT, H<sub>2</sub> and MeOH. The specific investment cost for SNG is shown separately in Figure 7 as the scale of the y-axis differ significantly compared to Figure 6.

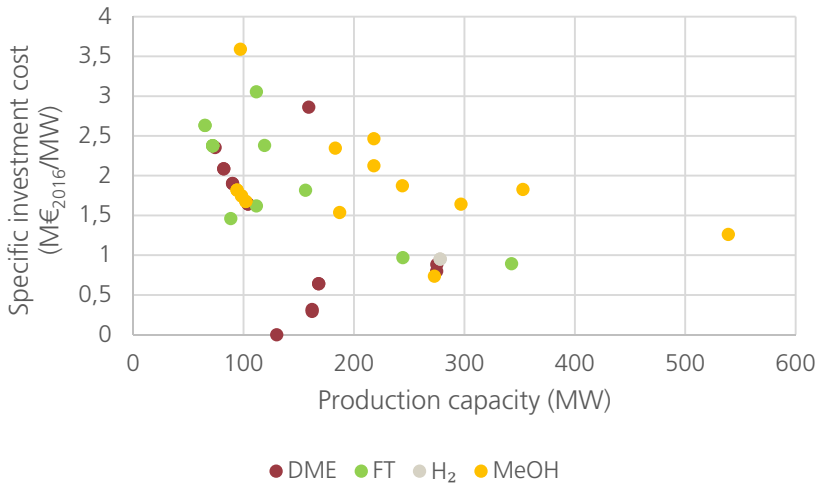


Figure 6 Specific investment cost for DME, FT, H<sub>2</sub>, and MeOH production plants

An economy-of-scale effect can be seen in Figures 6 and 7, as expected. The relationship between investment cost and capacity is more pronounced in the cases of DME and SNG. The greatest spread in specific investment cost was found for SNG production, Figure 7, where the cost ranged from M€ 62.3 to 1.1 per MW produced. It should, however, be borne in mind that seven of the eight cases stem from the same publication, and are therefore based on the same economic assumptions. The spread is much less for the other three fuels, ranging from M€2.4 to 0.3 per MW for DME, M€3.7 to 0.9 per MW for FT and M€3.6 to 0.7 per MW for MeOH. It is also interesting to note that the variation in data is greater, at least for FT and MeOH, between different studies at the same production capacity, than that expected from economy-of-scale effects. This variation can probably be attributed to the complexity of the technology (choice of reactors, downstream equipment, etc.) and, to some extent, the choice of data used to

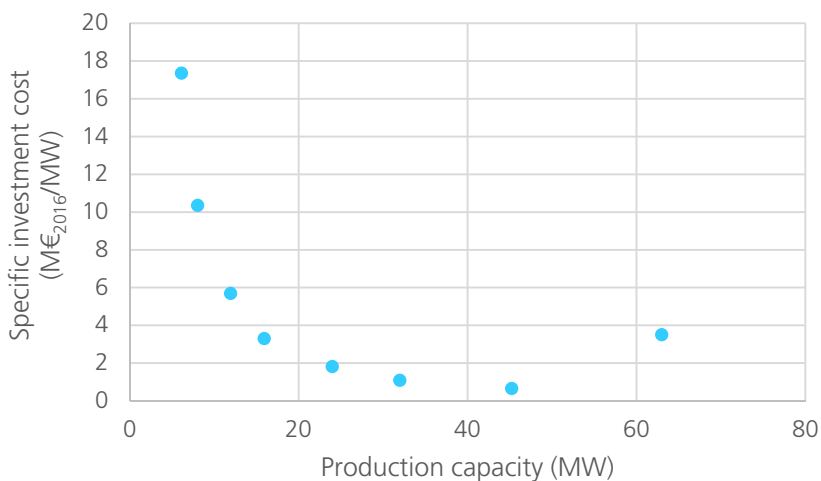


Figure 7. Specific investment cost for SNG production plants

calculate the investment costs. Some of the investment costs cited date back to the early 1990s, and it is unlikely that an index update will accurately reflect the evolution of cost over such a long time. The process configurations for DME and MeOH production are more standardized, with fewer design options, compared to those used for FT, which should lead to more consistent specific investment costs, however, this was not seen from the data analysed.

The operating costs are required to determine the production cost of a specific fuel. The investment cost usually represents 10-50% of the cost per tonne of fuel produced, and it is therefore important to review the input parameters chosen to calculate the operating cost, mainly for biomass and electricity, which represent the greatest proportion of the operating cost. Values of operating costs were collected from for each publication and the average, maximum, minimum and standard deviation determined (see Table 8).

**Table 8. Investment and operating parameters. SD – standard deviation**

	Average	Min	Max	SD
<b>Biomass (€/MWh)</b>	15.5	4.9	28.0	6.3
<b>Electricity (€/MWh)</b>	50.4	25.0	68.0	15.1
<b>Depreciation (years)</b>	20.7	10	25	4.6
<b>Weighted average cost of capital</b>	8.7%	4.1%	13.1%	1.4%

As can be seen from Table 8, the maximum cost of the biomass is €28 per MWh and the minimum €4.9 per MWh (the average being €15.5 per MWh). This is quite a large range, which is also reflected in the standard deviation, being almost half the average value, and not unexpected given the diverse nature of biomass. The cost of electricity is about €50 per MWh. Since the cost of feedstock and the cost of, and revenue from, electricity are the major costs in the production of synthetic fuels from biomass, the differences in economic performance between the studies can largely be explained by the differences in the cost of the feedstock and the assumptions made. There is a high degree of consensus on the depreciation of these types of plants, being about 21 years. There were some outliers, for example, the minimum value of 10 years, but the standard deviation is less than 5 years. There is also little deviation from the weighted average cost of capital.

However, the differences in the cost of biomass are not sufficient to explain the resulting differences in the production cost. In fact, the variations in production costs for the studies listed in Table 7, when using the average values as input (as in Table 8), are substantial (see Table 9). In these calculations, the output primary fuel was used as the basis. The production and use/demand of other consumables and side-products were resolved using the average cost of these. In the case of co-production, both the fuels were used as the basis for the calculations. In one case, [37] the protein was also considered a product.

**Table 9. Variation in production costs (€/MWh). SD – standard deviation**

	No. cases	Average	Min	Max	SD
<b>DME</b>	15	51	24	67	15
<b>FT</b>	17	67	34	133	25
<b>H<sub>2</sub></b>	3	61	49	84	20
<b>MeOH</b>	16	64	41	120	25
<b>SNG</b>	8	325	48	1154	98
<b>Co-production</b>	3	86	72	98	13

The data for the production of FT diesel, MeOH and DME are better, representing 17, 16 and 15 cases, respectively. It is clear that the production of DME is quite favourable on an energy basis as the average value is the lowest of the three: €51 per MWh. This is not much higher than the cost of producing crude oil, which at a price of US\$70 per bbl is equivalent to €48 per MWh; although it should be remembered that refined products are of higher value than crude oil. Methanol is more expensive to produce by gasification than DME, being €64 per MWh, and FT diesel is most expensive, €67 per MWh. These results are to be expected as the investment costs are higher for FT plants and methanol plants. However, the differences in investment costs



do not account for all the differences in the resulting production costs. The rather large ranges in data result in standard deviations that are quite high. This is particularly true in the case of SNG production, where the production cost varies from €48 to 1154 per MWh. However, it should be pointed out that all but one of these values are based on a single study, and thus the average value does not represent the average from several studies. In the case of DME, the cost of production ranges from €36 to 66 per MWh, while the range for MeOH is €39-89 and for FT-diesel €42-92 per MWh.

## 5 Conclusions

Several different concepts for industrially integrated biomass gasifiers were studied. However, although these concepts are the subject of academic research and evaluation, little or no interest has been shown by industry. This could be due to the lack of proof-of-concept facilities or unwillingness to risk high investments without long-term government incentive structures. From the point of view of gasification, integrated options may be better than stand-alone plants, however, industry might not regard the benefits to be sufficient to invest in new technology.

### 5.1 Literature review

In this meta-study, 35 publications covering a total of 138 cases of industrially integrated biomass gasification processes for the production of biochemicals and/or biofuels have been reviewed. It was found that most of the work performed in this field has been carried out by Swedish research groups, and that most of the cases studied are the gasification of black liquor in chemical pulp and paper mills for the production of various biofuels. The literature search revealed that research groups in other countries tend to focus on stand-alone biomass gasification plants. The reason for this geographical difference could be the combination of the availability of forest-based biomass and generous tax incentives for the production of renewable fuels, together with a long tradition of process integration in Sweden. Surprisingly, very few studies were found on other forest-based processes, for example, sawmills. In addition, very few studies among those reviewed dealt with the production of chemicals. This is probably because the production of chemicals from forest residues/by-products is still in its infancy, and the policy instruments in the most represented country (Sweden) favour the production of biofuels.

To determine the origin of the technical and economic data used in the reviewed publications, the references cited in each study were investigated. It was found that most of the studies were connected in a large citation network due to the use of a similar

base of data. This is not necessarily deleterious with regard to the technical data, as the technology in question has changed relatively little over recent decades. The same, however, cannot be said of the economic data, which were found to be both uncertain and outdated. There is a clear need for new estimates from industry, to enable reliable economic analysis of these types of systems in the future.

## 5.2 Meta-analysis

We have taken into account the problems associated with comparing system efficiencies reported in different studies. In order to circumvent this problem, the electricity equivalent method was used to recalculate values on an equal basis. In most cases, EE was higher than SE. This means that the systems convert low-exergy input into high-exergy output, resulting in high efficiency. When studying the energy carrier distribution within individual studies more closely, it was found that cases with electricity as output, as opposed to input, had a much higher EE than SE.

We found a considerable spread in the production costs and investment costs, even when normalizing them to a single input array of values. The variation in the production costs were often higher than the lowest production cost, leading to imprecise cost predictions.

This study confirms the fact that it is difficult to evaluate and compare techno-economic concepts. Recalculating the results to allow comparison on an equal basis still only provides indications at best, due to the lack of detailed process descriptions and heat and mass balances.

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# Paper III





# Regenerative reverse-flow reactor system for cracking of producer gas tars

Per Tunå · Fredric Bauer · Christian Hulteberg ·  
Laura Malek

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**Abstract** The gas produced in a biomass gasifier contains high amounts of tars which have to be removed prior to downstream utilization. Calcined dolomite is catalytically active for tar cracking reactions and resistant to sulfur poisoning. In this study, calcined dolomite was used as bed material in a reverse-flow reactor for cracking of tars in a model synthesis gas. 1-methylnaphthalene was used as model tar compound at a concentration of 15,000 mg/Nm<sup>3</sup>. The reactor system was operated at temperatures between 700 and 850 °C in the active zone. Total tar conversion was over 95 % for the system under reverse-flow conditions at the highest temperature. Already at the lowest temperature, up to 78 % of the 1-methylnaphthalene was converted, but mainly to other more stable tar compounds such as naphthalene and benzene, reaching a total tar conversion of only 23 %. To produce tar-free gas, higher temperatures are thus needed. The use of very high temperatures does, however, lead to a significant decrease in the specific area of the dolomite, as shown by BET surface measurements. The dolomite was further characterized with x-ray diffraction and energy dispersive spectroscopy.

**Keywords** Biomass gasification · Tars · Tar removal · Dolomite

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P. Tunå · F. Bauer (✉) · C. Hulteberg · L. Malek  
Department of Chemical Engineering, Lund University,  
P.O. Box 124, 221 00 Lund, Sweden  
e-mail: fredric.bauer@chemeng.lth.se

## 1 Introduction

The production of the next generation of bio-fuels is based on utilizing non-food crops, e.g., agricultural waste, forest residues, and energy crops [1]. One important process for the efficient utilization of such feed stocks is gasification, a technology originally developed for processing fossil fuels such as coal. In the gasification process, the feedstock is partly oxidized and the solid feedstock is reacted into a gaseous fraction and a solid ash fraction [2–4]. The composition of the gas depends on the type of gasifier, operating conditions, and feedstock, but it mainly contains CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, and N<sub>2</sub>, if air is used in the gasifier. Nevertheless, the gas also contains some lower hydrocarbons, tars, and trace amounts of contaminants such as NH<sub>3</sub>, H<sub>2</sub>S, and HCN [5]. A significant share—approximately 50 %—of the heating value of the producer gas is available in the lower hydrocarbons and tars, depending on gasifier type and process conditions [6].

The tar compounds formed does, however, constitute a well-known problem, as these compounds limit the utilization of the gas in many applications. The tars can condense in piping and/or harm downstream materials and equipment. Removal or conversion of these tar compounds is thus a priority to ensure the successful large-scale deployment of biomass gasification processes. Yet, there is not one clearly accepted definition of the word tar in the context of biomass gasification, although the definition by Evans and Milne<sup>1</sup> is often used and suits the purposes also of this study [7]. The tar compounds may further be characterized as primary, secondary, or tertiary [8]. Primary tar compounds are products derived directly from cellulose, hemi-cellulose, or

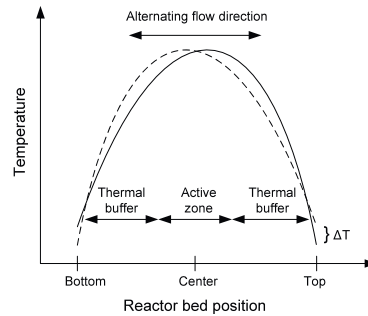
<sup>1</sup> The definition of Evans and Milne states that “the organics, produced under thermal or partial-oxidation regimes (gasification) of any organic material, are called ‘tars’ and are generally assumed to be largely aromatic.”

lignin, thus having high oxygen content; secondary tar compounds consist of phenolics and olefins; tertiary tars are either condensed tertiary tars—e.g., poly-aromatics without substituent groups—or alkyl tertiary tars, such as methyl derivatives of poly-aromatics.

Different approaches to tar removal in producer gas from biomass gasifiers have been investigated; physical as well as thermal and catalytic methods to eliminate or separate the tar from the producer gas [9]. Due to the high-energy content in the tars, it is preferable to decompose the tars to other gas compounds rather than to scrub or otherwise physically remove the tars from the gas. Thus, catalytic methods for tar conversion and decomposition have been thoroughly studied and reviewed [10–13]. Common Ni-based catalysts perform well in the tar cracking application and are available at relatively low costs, but a major disadvantage is their high sensitivity to sulfur compounds which are inevitably present in producer gas. The use of dolomite and olivine as catalysts for tar cracking has also been investigated, both as active catalyst particles in fluidized bed gasifiers and for downstream treatment [14–17]. To enhance the activity of the non-metallic catalysts Ni-olivine catalysts have also been proposed and tested with good results, although the deactivation effects after longer times on stream are still unclear [18–20]. As the tar content depends largely on the reaction conditions in the gasifier [21], the optimization of gasifiers to yield a gas with a low tar content has also been investigated thoroughly, and reviewed recently [22, 23].

In a regenerative reverse-flow system, heat is transferred between the fluid passing through the reactor and the stationary reactor bed, heating the bed and cooling the fluid. The bed acts as a thermal buffer, and when the flow is reversed, this heat is exchanged with the gas entering the reactor from the new direction. Thus, two alternating thermal buffer zones are created with an active zone in between, as seen in Fig. 1. This mode of operation enables a very high-thermal efficiency, up to 95 % [24]. An in-depth description of reverse-flow reactor systems, suitable applications, and important aspects of the operation of such systems was published by Matros and Bunimovich [25]. Reverse-flow reactors have traditionally been applied to exothermic processes such as regenerative thermal oxidation and regenerative catalytic oxidation used for VOC abatement, oxidation of SO<sub>2</sub>, and partial oxidation of methane for syngas production. The concept has, however, also been shown to be applicable to endothermic reactions, such as dehydrogenation of ethylbenzene [26].

A reverse-flow reactor for tar cracking, the first reverse-flow process combining an exothermic and an endothermic reaction, has been demonstrated earlier [27]. The reactor was filled with bauxite in the thermal buffer zones and catalytically active calcined dolomite in the active zone, operated at very high temperatures, about 1,050 °C, which leads to large



**Fig. 1** Alternating temperature profile with two thermal buffer zones and an active zone in a regenerative reverse-flow reactor

energy losses and increases the risk for soot formation. The lower hydrocarbons present in producer gas will, at high temperatures, form soot in the presence of oxidizers [28].

The aim of the research presented in this paper has been to provide proof of concept for a regenerative reverse-flow reactor for tar reforming, operating at temperatures below 1,000 °C and using a model producer gas with 1-methylnaphthalene (1-MN) as a model compound for tertiary tars. The lower operating temperature ensures that the methane present in the producer gas is not reformed, which is important if the objective of the gasification is to produce synthetic natural gas (SNG). By addition of pure oxygen at temperatures of about 800 °C, the tar is converted to syngas components by reforming and partial oxidation. By also retaining the methane content of the gas, a higher efficiency of the complete process (biomass to SNG) can be achieved as a higher share of the total energy content is utilized and methane is not first reformed and thereafter, resynthesized.

## 2 Materials and methods

### 2.1 Experimental setup

The experimental setup used for the tar reforming experiments is shown in Fig. 2. The reactor is vertically oriented and constructed from a Sandvik 253 MA high-temperature steel tube with an outer diameter of 152 and a length of 700 mm. Five smaller steel tubes are inserted into the reactor from the top and the bottom, one is used as a thermocouple pocket, welded shut in the reactor center, and four are used as diffusers for oxygen injection. The oxygen diffusers enter the reactor from a manifold at each end of the reactor. As the reactor is constructed for reverse-flow operation, the construction is completely symmetrical. The reactor is filled with Swedish dolomite (from Sala) particles with a size of 1–3 mm. Dolomite was chosen as it is easily available at low

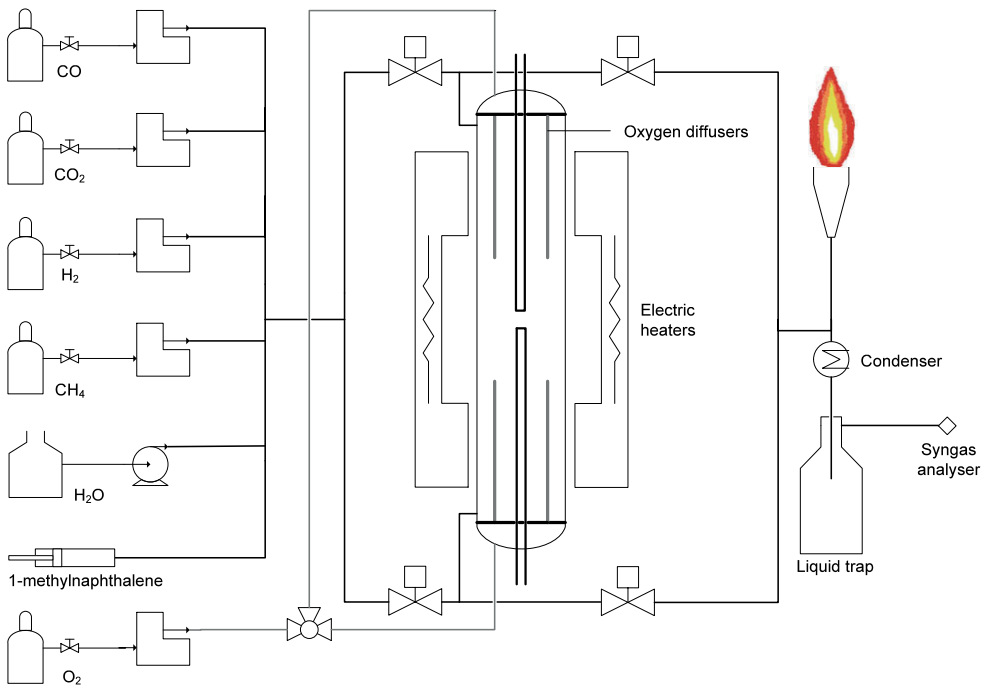
cost and suitable to fixed-bed operation, thus being a good choice for this kind of setup. The size of the dolomite particles was chosen to yield a balance between a large surface area and a low-pressure drop over the reactor. Furthermore, it is crucial to minimize the void volume to suppress the formation of flames. The dolomite bed and the effective reactor length, is 620 mm. The reactor is insulated with ceramic half-shell insulation modules. The shells covering the middle part of the reactor have integrated heating elements with a capacity of 3,500 W. Additional to the external heating, the reactor bed is heated by combustion of methanol before operation. At sufficient temperature ( $>200$  °C) methanol is injected together with  $H_2$ ,  $N_2$ , and  $O_2$ , which heats the reactor bed to the desired operating temperature, at which, the methanol flow is exchanged for water.

Process gas inlets are 19-mm steel tubes connected to the top, and bottom of the reactor. The flow direction is controlled using four electromagnetic valves. The gas flow is controlled by digital mass flow controllers and the water flow is controlled by a peristaltic pump. 1-MN is injected into the gas stream using a syringe pump. The oxygen flow

direction is controlled by an additional three-way valve and is via the manifold distributed to the diffusers which inject the oxygen 240 mm into the reactor bed. Oxygen is injected co-current with the process gas, creating a hot, active zone slightly shifted from the center of the reactor. When the flow direction of process gas and oxygen is reversed, the temperature of the former active zone decreases due to endothermic reforming reactions, heat transfer to the reactor ends and heat losses, whereas a new active zone is formed in which the temperature increases. The active zone in the reactor is defined as beginning at the oxygen inlet and ending about 100-mm downstream, as this is where the temperature starts to drop significantly. The reactor operating temperature was defined as the average temperature measured in the active zone.

## 2.2 Experiments

The reverse-flow tar reformer was operated at active zone temperatures of 700, 800, and 850 °C, measured as the average temperature in the active zone. Flow rates of 0.5, 0.85, and 1.2  $Nm^3/h$  were applied, corresponding to gas



**Fig. 2** The experimental setup

hourly space velocities of 45, 75, and 105 h<sup>-1</sup> and residence times of 29, 17, and 12 s. Before operation with the model producer gas, the reactor was heated to a maximum temperature of 900 °C in the active zone for 15 h to calcine the dolomite bed. The reactor was then operated for a minimum of 1 h at each temperature and flow rate. The total time on stream for the reactor was approximately 40 h. The reactor, which is rather large for laboratory testing purposes, can most probably be used with higher flow rates. The mass flow controllers limited the testing of the reactor at higher flow rates, as they were not designed to handle larger flows. As seen in Fig. 2, the model producer gas was mixed from separate bottles of gas, instead of using a premixed gas. Into this model producer gas, the model tar compound 1-MN was injected, at a ratio of 15,000 mg/Nm<sup>3</sup>. The composition of the model producer gas is shown in Table 1.

### 2.3 Analysis and characterization

As seen in Fig. 2, a share of the gas exiting the reactor system is flared, giving an indication of some of the gas properties; varying flow rates yield a flame with changing flame height and a gas containing hydrocarbons with C–C bonds burn with a yellow flame, whereas a gas with only CO, H<sub>2</sub>, and CH<sub>4</sub> is faintly blue, giving an immediate indication of the performance of the tar reformer.<sup>2</sup> Thus, operating conditions yielding yellow flames are easily discarded as non-productive.

The gas after tar conversion was sampled and analyzed using a method developed at the Swedish Royal Institute of Technology [29]. One hundred milliliters of the process gas that is to be analyzed is sucked through a matrix of 500-mg aminopropyl bond silica during a period of approximately 60 s. The sample is then eluted from the matrix by first adding 100 µl of an internal standard consisting of 2.5 mg/ml tert-butylcyclohexane in dichloromethane (DCM). An additional 2 ml of DCM is then added and the solvent is pressed through the matrix into a glass vial with a flow rate of 1–2 ml/min using nitrogen gas. After elution, the sample is analyzed using gas chromatography to identify and quantify the tar compounds in the gas. A reference sample was also analyzed, i.e., a sample of gas with tar that was not passed through the reactor. The 1-MN conversion was then calculated as the response of the 1-MN content in the gas sample compared with the response of 1-MN in the reference sample. Total tar conversion was calculated as the response of all the identifiable tar compounds compared with the response of 1-MN in the reference sample.

The bed particles were analyzed for changes in their Brunauer–Emmett–Teller (BET) surface areas measured by the adsorption of nitrogen at liquid nitrogen temperature

<sup>2</sup> A movie showing the flare is available as electronic supplementary material.

**Table 1** Composition of the model producer gas

Component	Volumetric fraction
CO	25 %
CO <sub>2</sub>	15 %
H <sub>2</sub>	25 %
CH <sub>4</sub>	10 %
H <sub>2</sub> O	25 %
1-Methylnaphthalene	15,000 mg/Nm <sup>3</sup>

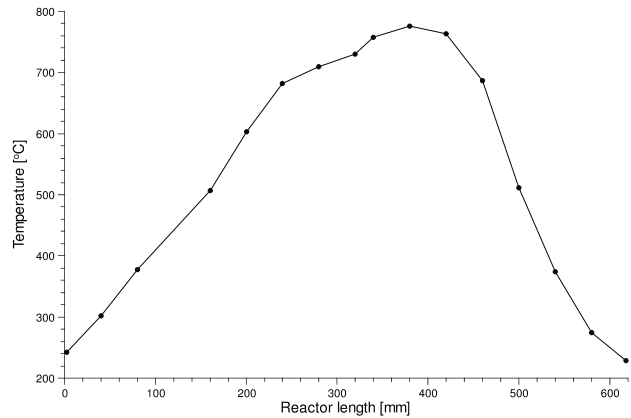
using a Micromeritics ASAP 2400 instrument after degassing for 16 h at 350 °C. Pore volume analysis was performed using the BJH method [30]. The Halsey formula [31] was used to calculate the thickness of the adsorbed layer (*t* value). The desorption-isotherm was used for the analysis; the average values of two analysis runs were used. The content of the bed particles was analyzed using x-ray diffraction (XRD) analysis, performed on a Seifert XRD 3000 TT diffractometer using CuK- $\alpha$  radiation and a rotating sample holder. The tube voltage and the current were set to 40 kV and 40 mA, respectively. The instrument was calibrated using a Si standard. Diffractograms were recorded between 5 and 80 ° 2 $\theta$  in steps of 0.05 ° (10 s/step). The elemental composition was analyzed from <200- $\mu$ m fragments from crushed catalyst particles, using energy dispersive x-ray spectroscopy (EDS) in a scanning electron microscope (SEM) operated at 15 kV.

## 3 Results and discussion

### 3.1 Reactor operation

The reactor was operated successfully at temperatures up to approximately 850 °C in the active zone. As the thermocouples were placed inside a steel tube along the center of the reactor tube, it is possible that single hot spots reached higher temperatures than that measured by the thermocouples. A temperature profile for the reactor operating at 750 °C (as defined in Section 2.1) is shown in Fig. 3. As described earlier, the oxygen is injected at 420-mm reactor length. The temperature profile thus shows that mixing of oxygen and fuel gas is not instant since the temperature increases for about 50 mm, indicating exothermic reforming and combustion reactions taking place.

However, a few problems were experienced which were most probably due to the reactor bed and the diffusion of oxygen and feed gases inside it. When heating the reactor by combustion of methanol, the combustion was incomplete when the reactor was operated at top-to-bottom flow, whereas complete conversion was reached when the flow direction was reversed. This is most probably the effect of the oxygen diffusers entering from the top, being unevenly packed with dolomite particles, creating a larger flow of oxygen in one of

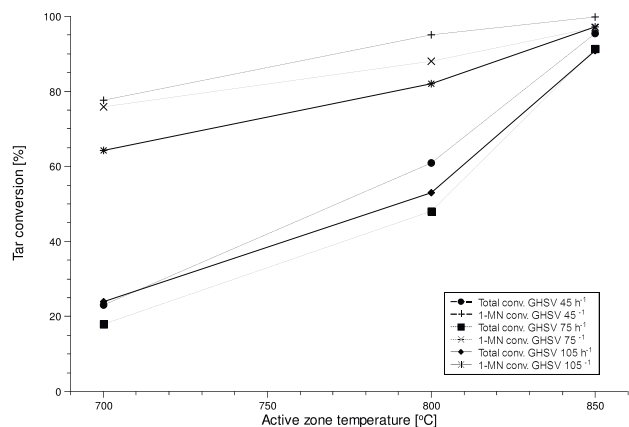
**Fig. 3** Temperature profile of the reactor operating at 750 °C

the diffusers and thus not reaching an even concentration gradient along the vertical reactor axis. It is possible that with smaller bed particles, it would be easier to pack the reactor bed more evenly and reduce these problems, although this would also increase the pressure drop over the reactor. This is, however, not believed to have had a major influence on the tar reduction experiments.

### 3.2 Tar cracking

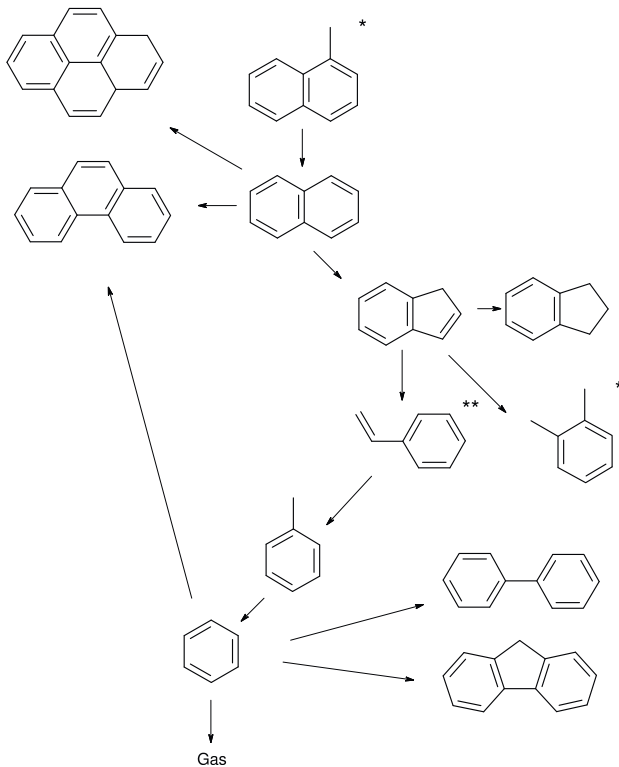
The regenerative reverse-flow system showed good conversion of 1-MN, up to 78 %, at temperatures as low as 700 °C (Fig. 4). At these low temperatures, the 1-MN was, however, not reformed to syngas compounds, but mainly rather to other, lighter

tar compounds such as benzene, toluene, xylene, indane, indene, several unidentified species and—predominantly—naphthalene. Apart from these light tar compounds, there are also trace amounts of heavier compounds such as phenanthrene, fluorene, pyrene, and other unidentified species. The total tar conversion, i.e., conversion of both 1-MN and its derivatives such as toluene and naphthalene, at 700 °C was no higher than 24 %. Furthermore, at 700 °C, more naphthalene than 1-MN was present at the reactor outlet. This is an indication that the initial step in the decomposition of 1-MN is the separation of the methyl group from the aromatic rings, which is to be expected as the aromatic ring structure is very stable (Fig. 5). With increasing temperature in the active zone of the reactor, the conversion of 1-MN increased slowly, whereas the total tar conversion

**Fig. 4** Total tar conversion and conversion of 1-MN at tested temperatures and flow rates



**Fig. 5** Reaction scheme for the conversion of naphthalene to the species identified in the gas from the reverse-flow reactor, adapted from [33]. 1-MN and xylene (\*) were not included in the original figure, whereas the important intermediate styrene (\*\*) could not be identified although it most likely exists in the gas, probably due to detection and identification difficulties

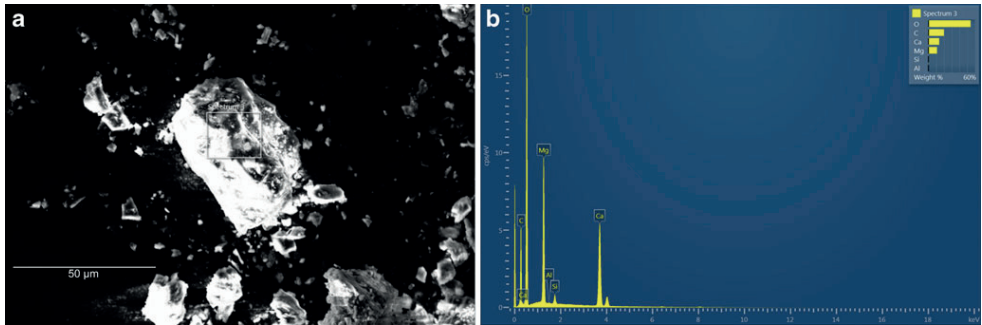


increased rapidly. The increase in total conversion is almost entirely because of increased naphthalene conversion. At 850 °C, the total tar conversion was as high as 95 %, with a 1-MN conversion of more than 99 % for the lowest flow rate (Fig. 4).

Several other studies [32–34] have identified naphthalene as being one of the most difficult tar compounds to crack, which is to be expected as the aromatic ring structure is very stable. The tar cracking mechanism is very complex and difficult to map, but the results from this study with fast

**Table 2** Composition and BET surface area of the fresh and used dolomite

Catalyst sample	BET surface area [m <sup>2</sup> /g]	BJH cumulative desorption area of pores [m <sup>2</sup> /g]	BJH cumulative desorption volume of pores [cm <sup>3</sup> /g]
Fresh dolomite	0.26	0.25	0.00084
Calcined 700 °C	22	29	0.14
Calcined 800 °C	18	20	0.17
Calcined 900 °C	9.3	8.5	0.030
Producer gas inlet	8.0	11	0.070
Between inlet and oxygen 1	1.9	2.1	0.0057
Between inlet and oxygen 2	0.94	0.90	0.0018
Oxygen inlet	0.31	0.29	0.0020
Middle	0.36	0.11	0.00020



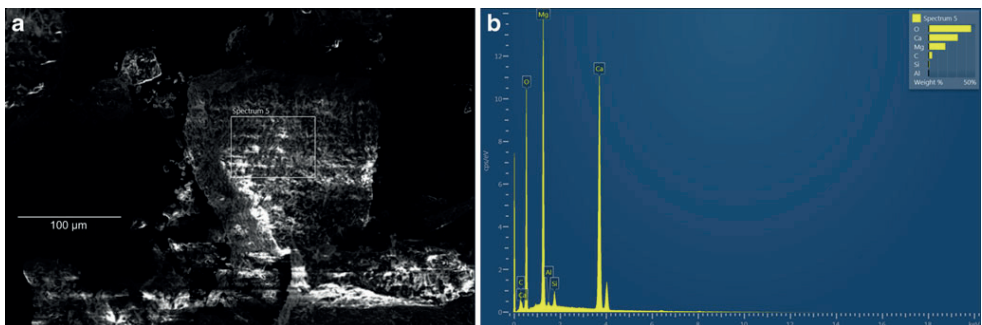
**Fig. 6** Fresh dolomite sample, **a** showing a SEM image of the sample and **b** showing the EDS spectrum of a selected area of the sample

conversion of 1-MN but high contents of naphthalene left in the gas at the lower temperatures align well with observations by others. Aldén et al. showed that most of the tars in the producer gas are easily converted with dolomite at 800 °C but that BTX, naphthalene, biphenyl, phenanthrene, and pyrene remains [32]. Coll et al. showed that the reactivity of the aromatic compounds decrease with the number of rings in the molecular structure with the exception of naphthalene which is very difficult to convert, i.e., the order of reactivity is benzene > toluene » anthracene » pyrene > naphthalene [35]. Garcia and Hüttinger [33] proposed a reaction scheme for the steam gasification of naphthalene which is applicable to naphthalene cracking, in which one of the aromatic rings is broken forming indene, from which styrene, toluene, and subsequently, benzene are formed. The dolomite is most probably active in forming naphthalene radicals by hydrogen abstraction, i.e., the initiating step in breaking the aromatic ring of the naphthalene, but that the cracking process is inhibited by the hydrogen present in the gas as this will easily react with the naphthalene radical and reform naphthalene

[32]. With the experimental setup used for this study, it was not possible to calculate the conversion of methane; it is, however, believed to be very low due to the very high temperatures usually needed to reform methane.

### 3.3 Catalyst characterization

The catalyst samples in Table 2, with the exception of the fresh catalyst, were taken from different positions along the reactor length, from the inlet to the middle. The fresh dolomite had a BET surface area of 0.26 m<sup>2</sup>/g whereas the used dolomite had an area between 0.31 and 8 m<sup>2</sup>/g. The initial surface area is lower than what has been found in the literature [17, 36–38], which is usually in the 0.5–10 m<sup>2</sup>/g range. Dolomite samples were calcined at 700, 800, and 900 °C. The calcination seems to activate the dolomite and at first, significantly increases the surface area of the material. With increasingly higher calcination temperature, the surface area does, however, decrease due to sintering of the material, with is also in line with the results found in the literature. The BET surface area and the pore



**Fig. 7** Dolomite sample from the reactor center, **a** showing a SEM image of the sample and **b** showing the EDS spectrum of a selected area of the sample

volume clearly shows how the catalyst is sintered as it gets procedurally hotter in the reactor bed from the producer gas inlet to the oxygen inlet and the surface areas are well in line with what has previously been reported in the literature at these conditions [36–38]. The decrease in surface area and pore volume is, however, much larger in the dolomite samples from the reactor than in the samples which were calcined separately at 900 °C. This indicates that the temperature in the reactor not only may have been higher than the temperature measured by the thermocouples, leading to severe sintering, but also that the pores may be blocked by depositions formed during operation. This means that after a longer time of operation, only the outer particle area may be active for the tar cracking as all pores are blocked. The effect of this on cracking efficiency must be further studied and the reactor temperature must be carefully controlled.

The catalyst composition was determined with EDS in a SEM. Figures 6 and 7 shows SEM images of the dolomite surface and the EDS spectrum from the marked area in the SEM image, showing the content of Ca, Mg, O, C, Si, and Al in the dolomite. The literature reports a growing particle size with increasing temperature, something that has been indicated also in this investigation, but more images and samples would have to be taken to statistically confirm this [37].

The EDS analysis reported in Figs. 6 and 7 show different results compared to the XRD analysis, hence, there is a difference between the bulk and the surface composition. The XRD analysis confirmed the presence of both calcined and uncalcined dolomite (oxide form) in the reactor center, from before one oxygen inlet, throughout the reactor to after the second oxygen inlet. The XRD analysis was qualitative and revealed the presence of  $\text{CaMg}(\text{CO}_3)_2$  as well as  $\text{CaO}$  and  $\text{MgO}$ . The relative quantities of each of these forms could, however, not be measured with the equipment. However, the dolomite analyzed with EDS and shown in Figs. 6 and 7 is clearly calcined, with a very low carbon content showing that the  $\text{CO}_2$  has dissociated from the mineral, and contains more magnesium than calcium at the analyzed surfaces. This surface concentration is well in line with other literature findings [37]. The increased Mg concentration on the surface of the dolomite grains is interesting as it has been speculated that the surface oxygen atoms are responsible for hydrogen abstraction [32]. This speculation has been founded on an analogy with methane reforming over  $\text{MgO}$  and the higher the Mg surface concentration, the more likely this is to represent the true mechanism of the tar decomposition.

#### 4 Conclusions

A novel system comprising a regenerative reverse-flow reactor with a dolomite bed for reforming of tars in producer gas

from biomass gasification has been developed. The system was tested using a model producer gas and a single model tar compound, 1-methylnaphthalene, resulting in a total tar conversion of up to 95 % at 850 °C operating temperature in the active zone, with an inlet concentration of 1-MN of 15,000 mg/Nm<sup>3</sup>. Although the conversion of 1-MN was up to 78 % already at 700 °C, the analysis shows that it is mainly converted to other tar compounds, e.g., naphthalene and benzene, resulting in a total tar conversion of only about 28 %. An operating temperature above 800 °C is thus necessary for efficient operation. The high-thermal efficiency of the system promises a highly efficient process step for integration in a gasification process train. The catalyst characterization showed that not all of the bed material in the reactor center was calcined and that the bed contained several phases of both carbonated and oxidized calcium and magnesium. The surface area of the catalyst decreases by almost 100 times and not much surface area remains on the active catalyst.

Future work should be performed on producer gas from a real gasifier. There are many important compounds present in producer gas that were not present in this study, for practical and safety reasons, such as benzene, ethylene, and ammonia, which could have a significant impact on downstream process equipment. Other aspects to investigate are the effects of reactor bed particle size, higher flow rates, improved diffusion of oxygen in the reactor, and the effect of continuous operation for a long time on the bed material.

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# Paper IV





# Scrubber liquid recovery in biomass gasification plants: centrifugation as a method for tar separation

Laura Malek<sup>1</sup> · Christian Hulteberg<sup>1</sup> · Helena Svensson<sup>1</sup>

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**Abstract** Many gasification plants use scrubber systems for the removal of tars from producer gas. The cost of the scrubber liquid represents a considerable part of the operating cost, which could be decreased by regenerating the spent scrubber liquid by separating it from ash residues and heavy tars. In this study, different types of spent scrubber liquids were regenerated using a centrifuge. The effect of centrifugation time (1.5–10 min) and sample temperature (50–90 °C) on the separation efficiency was studied. Based on the results, the separation of tars from the scrubber liquids can be ranked as follows: diesel > RME > linoleic acid > linseed oil > rapeseed oil > motor oil. This ranking correlates to the viscosity of the different scrubber liquids, with the separation efficiency increasing with decreasing scrubber liquid viscosity. The best separation efficiency was achieved for scrubber liquids with low viscosity at 90 °C and 10 min of centrifugation time. The results obtained indicate that centrifugation can be used for the regeneration of spent scrubber liquid.

**Keywords** Biomass tar · Scrubber liquid · Centrifugation · Regeneration

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✉ Laura Malek  
laura.malek@chemeng.lth.se

<sup>1</sup> Department of Chemical Engineering, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

## 1 Introduction

Biomass has a considerable potential for the production of renewable energy and chemicals as it can be converted into a wide range of end products using various conversion technologies, such as gasification, pyrolysis and fermentation. Unfortunately, due to high biomass and auxiliary costs, the selling price of the end products is not yet competitive compared to their fossil-based counterparts. The production cost of products that are produced through biomass gasification varies depending on the price of the feedstock and the operating cost for gas upgrading and waste disposal. A very important, but often expensive, step in biomass gasification is the removal of impurities such as particles and tars from the producer gas, i.e. the gas leaving the gasifier. The concentration of tars in the producer gas must be reduced before the gas can be used in downstream processes, as tars may condense and cause fouling, blockage and damage to equipment such as filters, engines, turbines, etc. [1]. The cost of gas cleaning varies depending on the required purity of the gas, which, in turn, depends on the end application. A high purity is often required in processes that use producer gas for chemical synthesis, while gas used as fuel in boilers or engines for electricity production in combined heat and power plants (CHPs) can contain a higher level of impurities. Thus, lowering the operating cost of gas cleaning enables the production of economically viable renewable energy and chemicals through biomass gasification.

Various technologies are currently in use for tar removal, and these can be divided into two categories: mechanical/physical removal, i.e. scrubbing and filters, and thermal/chemical conversion, i.e. cracking, reforming and partial oxidation [1–5]. Both categories have advantages and disadvantages. Although thermal/chemical conversion methods



transform the tars into components that can be used in the process, the process must be carried out at high temperatures, and they thus require high amounts of energy [3]. Mechanical/physical removal methods are usually more technically and economically attractive due to their simpler design [6]; however, they create waste.

Scrubbing is widely used in gasification plants [7, 8], but the cost of the scrubber liquid and its disposal once it has been used represents a non-negligible part of the operating cost. The operating cost of this part of the process could thus be reduced by regenerating and reusing the spent scrubber liquid. Numerous studies have been carried out on the absorption of volatile organic compounds (VOCs) and tars by various scrubber liquids. Silicone oil is frequently used for the removal of VOCs. Components of VOCs that have been studied together with silicone oil are toluene and xylene [9], toluene, dimethyl sulphide and dimethyl disulphide [10] and methyl ethyl ketone [11]. Heymes et al. [12] studied the absorption of toluene by silicone oil, polyethylene glycols, phthalates and adipates. Vegetable oil, lubricant oil and water were used by Ozturk and Yilmaz [13] for the removal of benzene, carbon tetrachloride, toluene and methanol. Pierucci [14] studied the removal of acetone, methyl ethyl ketone, ethyl acetate, toluene, butyl acetate and xylenes, but the type of oil used was not specified. Studies on the removal of biomass tar or model tar components have been carried out using vegetable oil [15]; vegetable oil and waste cooking oil [16]; diesel, bio-diesel, engine oil, vegetable oil and water [17]; and diesel, linseed oil and water [18].

While a great deal of work has been performed on the absorption of VOCs and tar, only two of the studies mentioned above considered the possibility of regenerating the absorption medium/liquid after use [11, 13]. Tar removal systems that include scrubber liquid regeneration are commercially available, such as the OLGA process developed by the Energy Research Centre of the Netherlands (ECN) [7]. The OLGA process consists of two separate scrubber columns for tar removal and a stripper column for scrubber liquid regeneration. Regeneration in this system is very effective, resulting in an outgoing producer gas of a very high quality, as a well regenerated scrubber liquid removes more impurities from the producer gas. However, despite its advantages, a producer gas of the high quality produced in the OLGA process is not required in all applications. A higher level of impurities may be desirable, for example, to increase the calorific value of the gas when used to produce energy. Such a gas could be produced by regenerating the spent scrubber liquid using a centrifuge instead of a stripper column. By doing this, only heavy insoluble compounds would be removed while lighter soluble compounds would accumulate in the scrubber liquid. Centrifuges have long been used in the coal tar and coke industry to separate different tar fractions [19, 20]. Regarding the removal of tar in biomass gasification plants,

Bartocci and Patterson [21] briefly mention using a centrifuge separator system to remove tar from the process oil. Also, a patent application for a centrifuge system for the removal of biomass tars from liquids was submitted in 2013 [22]. This technology is much simpler, cheaper to acquire and does not require the same energy input as that needed to operate a stripper column. Other alternatives to be considered for scrubber liquid regeneration are, e.g. sedimentation and crystallization [23]. While sedimentation would be an even simpler solution than centrifugation, the process is slow in comparison and would require large sedimentation tanks and larger volumes of scrubber liquid circulating in the system. Crystallization is a more complex technique that requires a higher energy input compared to a centrifuge.

This study examines the possibility of regenerating different types of spent scrubber liquid using a centrifuge. Model spent scrubber liquids were created using various scrubber liquids, water, wood tar and real tar/ash reject (sludge) from a small-scale biomass gasification CHP plant. Seven different scrubber liquids were investigated in the experiments. These liquids have been chosen based on the results of a literature review or because their chemical structure was believed to be suitable. The ability of the liquids to dissolve the sludge was investigated, and they were then centrifuged to investigate the possibility of scrubber liquid recovery. The effect of centrifugation time and temperature on the separation efficiency was studied.

## 2 Materials and methods

### 2.1 Materials

Seven different potential scrubber liquids were used in this study: diesel, linoleic acid, linseed oil, motor oil (10–50 W), silicone oil, rapeseed oil and bio-diesel, in this case rapeseed methyl ester (RME). Commercial wood tar made from pine wood (liquid), sludge and water were used in the experiments. The linseed oil, motor oil, rapeseed oil and wood tar were all purchased at the lowest price from grocery and hardware stores. The diesel was produced by Preem and was purchased from a petrol station. The linoleic acid (product number 62240) and silicone oil (product number 85409) were purchased from Sigma-Aldrich. Both the RME, provided by Wibax, and the sludge were obtained from a small-scale CHP plant in Sweden. For analysis and composition of the sludge, please refer to Sections 2.3.4 and 3.2. The commercial wood tar used (Furutjåra A) is manufactured by Claessons Trätjåra AB. Due to the complexity of the wood tar, no exact composition could be determined. It was however found, using the analysis described in Section 2.3.5, that the wood tar mainly consists of polar components such as carboxylic acids. The plant uses a cyclone gasifier, and the gas cleaning

train consists of a cyclone, an RME scrubber and a wet electrostatic precipitator.

## 2.2 Experimental methods

### 2.2.1 Preliminary testing of scrubber liquids

Preliminary experiments were performed to determine whether it was possible to dissolve wood tar and sludge in the selected scrubber liquids. Water was also added to determine whether the wood tar and sludge would remain in the scrubber liquid or transfer to the water phase. The method was developed based on previous work by Brage and Sjöström [24]. Scrubber liquid (50 g) was mixed with 5 g sludge and 5 g wood tar, to form a homogeneous mixture. Water (50 g) was then added, and the mixture was stirred by hand and was left to separate into clear phases (which took approximately 30 min) before assessment of the solubility in the scrubber liquid. The desired result was clear separation into two phases, scrubber liquid and water, with the wood tar and sludge remaining in the scrubber liquid.

### 2.2.2 Model spent scrubber liquid

Model spent scrubber liquids consisting of scrubber liquid, sludge, water and commercial wood tar were prepared for the separation experiments. As real spent scrubber liquid was only available for RME, model spent scrubber liquids were required for the obtained results to be comparable. In order for a fair comparison, with RME, to be possible, a model spent scrubber liquid for RME was also prepared. The composition and mixing ratios were determined by analysing the spent scrubber liquid from a small-scale CHP plant, see Table 1. The amount of sludge was estimated by centrifuging real spent scrubber liquid samples. As the sludge consists mostly of ash residue and heavy tars, liquid commercial wood tar made from pine was added to the model spent scrubber liquid. It was assumed that the commercial wood tar and the tar produced in the CHP plant had similar compositions, and therefore, the commercial wood tar would be a valid substitute for the lighter tar compounds not present in the sludge. The approximate amount of commercial wood tar needed was calculated by analysing tars from the real spent scrubber liquid. The results of this analysis were also used when defining light and heavy tars: heavy tars were defined as mostly polycyclic

**Table 1** Proportions of components in the model spent scrubber liquid

Component	Amount (wt%)
Scrubber liquid	50
Water	5
Wood tar	5
Sludge	40

aromatic hydrocarbons (PAHs) with a molecular weight above 300 g/mol. (The analysis method is further described in Section 2.3.5.) The water content was estimated using data for water solubility in commercial bio-diesel [25] since RME is used as the scrubber liquid in the CHP plant. The model spent scrubber liquids were prepared by weight using laboratory scales (Kern KB 1200-2 N, reproducibility 0.01 g and Mettler AE 260 Delta Range, reproducibility 0.5 mg). The components were mixed by hand until a homogeneous mixture was achieved, meaning that no lumps of sludge remained.

### 2.2.3 Centrifugation

Centrifugation was chosen for the separation experiments of the model spent scrubber liquids, and the effect of centrifugation time and temperature on the separation efficiency was studied. The model spent scrubber liquids were transferred to 15 mL glass centrifuge tubes, each sample weighing approximately 12 g, and heated in an oven to the desired temperature before being transferred to the centrifuge. A Thermo IEC Centra CL2 centrifuge was used to separate the model spent scrubber liquid samples. Two independent experiments were carried out for each sample under each set of experimental conditions, as specified in Table 2. Each combination of time and temperature was assigned a number, I–IX. The chosen temperature span 50–90 °C can be obtained in the CHP plant by heat exchange, and the time span 1.5–10 min represents reasonable residence times of the spent scrubber liquid in an industrial centrifuge suitable for the specific plant. The samples cooled to 30 °C during centrifugation due to 30 °C working temperature of the centrifuge. After centrifugation, the upper liquid phase of the samples was decanted by hand. The upper liquid phase and the solid lower phase remaining in the centrifuge tube were then weighed separately.

## 2.3 Analyses

### 2.3.1 Separation efficiency

The separation efficiency was determined by weighing the upper liquid phase (Phases 1 and 2 as described in Section 3.3) of the samples after centrifugation and comparing the result with either the total sample weight, to obtain the degree of separation (DOS), or the amount of scrubber liquid, to determine the scrubber liquid recovery. The DOS and scrubber liquid recovery are defined as:

$$\text{DOS \%} = \frac{m_{\text{Phase 1+2}}}{m_{\text{Total sample}}} \cdot 100$$

$$\text{Scrubber liquid recovery \%} = \frac{m_{\text{Phase 1+2}}}{m_{\text{Scrubber liquid}}} \cdot 100$$

A DOS of 100 % means that no separation of the sample occurs during centrifugation. Considering the composition of

**Table 2** Combinations of experimental conditions during centrifugation

Temperature	Time		
	1.5 min	5 min	10 min
50 °C	I	II	III
70 °C	IV	V	VI
90 °C	VII	VIII	IX

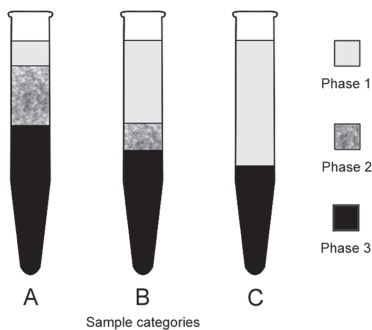
the model spent scrubber liquid (see Table 1), the desired results are Category C samples (see Fig. 1) with a DOS of 50 % and scrubber liquid recovery of 100 %. This would mean that the upper liquid phase only consists of recovered scrubber liquid, while the sludge, tar and water ends up in the bottom phase.

### 2.3.2 Sample loss

There was a small loss in sample mass during the separation experiments due to evaporation when heating the samples and losses during sample weighing. The sample loss was calculated for the scrubber liquids according to the following expression:

$$m_{\text{Sample loss}} \% = \left( \frac{m_{\text{Total sample}} - m_{\text{Phase 1+2+3}}}{m_{\text{Total sample}}} \right) \cdot 100$$

Table 3 gives the average and maximum sample loss for all scrubber liquids, with the exception of silicone oil (see Section 3.1). The reproducibility error of the Mettler AE 260 Delta Range scale (0.5 mg) is considerably smaller than the sample loss. The contribution of the scale to any error in the calculated results can thus be considered negligible.



**Fig. 1** Schematic illustration of the distribution of phases in the three categories A–C. Phase 1 consists of scrubber liquid and lighter tars dissolved in the scrubber liquid, Phase 2 is a mixture of Phase 1 and Phase 3 and Phase 3 is a solid phase consisting of heavy tars, ash and water

**Table 3** Sample losses

Scrubber liquid	Average (%)	Max (%)
Diesel	0.34	0.61
Linoleic acid	0.34	1.15
Linseed oil	0.25	1.26
Motor oil	0.51	2.68
Rapeseed oil	0.25	0.66
RME	0.29	0.88

### 2.3.3 Viscosity measurements

The viscosity of the fresh scrubber liquids was measured to determine whether there was any correlation between the viscosity of the liquid at different temperatures and the efficiency of separation of the model spent scrubber liquids. A Malvern Bohlin Visco 88 rotational viscometer equipped with a cup and bob combination, meeting the C30 DIN53019 standard, and a heating jacket were used for the measurements. The rotational speed of the bob was set to a constant 1000 rpm, to mimic the high rotational speed in a commercial industrially sized centrifuge, while the temperature was varied between 30 and 90 °C.

### 2.3.4 Analysis of sludge

The sludge was analysed to determine the composition. Samples of the sludge were dried at 110 °C for 50 h, and the samples were weighted before and after the drying using a Mettler AE 260 Delta Range scale to determine the mass fraction of water and lighter tar compounds. The solids content was determined by gravimetric analysis using a 1 µm filter. Tar content was measured according to the tar analysis method described in Section 2.3.5.

### 2.3.5 Analysis of tars

The upper liquid phases of the separated samples were analysed to determine whether the centrifugation time had an effect on the concentration of dissolved tar components. Samples of fresh scrubber liquids were also analysed for comparison. Dichloromethane was used to dilute the samples before they were separated into two fractions, a non-polar and a polar fraction, on a Supelco amino phase solid-phase extraction column. It was assumed that the non-polar fraction contained aliphatic and aromatic hydrocarbons, while the polar fraction contained acidic compounds such as carboxylic acids and phenols. The polar fraction was derivatized with N,O-Bis(trimethylsilyl)trifluoroacetamide and analysed with a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a Varian CP-1177 split/splitless capillary injector. Two columns were used: a CP-Sil 8CB MS

(25 m × 0.25 mm × 0.40 μm) column preceded by a guard column of intermediate polarity (2.5 m × 0.25 mm × 0.40 μm). Helium was used as the carrier gas at a flow rate of 1.3 mL/min. The inlet pressure was set to 15 psi, the injector temperature to 280 °C, the detector temperature to 300 °C, the injection volume was 1 μL and the split ratio was 1:100. The initial column temperature was maintained at 40 °C for 3 min before it was increased by 8 °C/min at constant flow to 310 °C, where it was maintained for 5 min. The phenolic tar components were quantified using internal standard calibration with 4-ethoxyphenol, and the measurement error was estimated to be ±10 %. Gas chromatography could not be used to analyse the non-polar fraction due to interference between the target analytes and the diesel and RME. Instead, the aromatic tar components were quantified using high-performance liquid chromatography with a K-2800 UV diode array detector (HPLC-UV-DAD) and external calibration with tert-butylcyclohexane. As with the gas chromatographic analysis, two columns were used: a Supelcosil LC-PAH (25 cm × 4.6 mm × 5 μm) column preceded by a guard column with a similar phase (5 cm × 4.6 mm × 5 μm). Water and acetonitrile were used as mobile phases, at a flow rate of 1 mL/min, and the sample injection volume was 10 μL. The initial acetonitrile concentration was maintained at 60 % for 1 min and was then increased to 100 % over 23 min and maintained for 10 min, before being decreased to 60 % over 45 min. The measurement error in this procedure was estimated to be ±10 %.

### 3 Results and discussion

The aim of this study was to examine the possibility of regenerating and recovering scrubber liquid in biomass gasification plants using a centrifuge. An ideal recovery process would completely remove the ash residues, water and heavy tars from the scrubber liquid, which could then be recirculated into the scrubber. For a complete recovery of the scrubber liquid, also, light tars need to be removed. However, this was not the aim of this paper and has therefore not been investigated. This means that the most desirable outcome of the separation experiments would be Category C samples (Fig. 1) with a DOS of 50 % and a scrubber liquid recovery of 100 %.

#### 3.1 Preliminary testing of scrubber liquids

The ideal result would be a clear separation into two phases, an upper phase of scrubber liquid containing the wood tar and sludge and a lower phase containing water. This was achieved for all the scrubber liquids with the exception of the silicone oil. In the case of silicone oil, three clear phases could be distinguished, with the tar/sludge mixture in the middle between the water and the oil phases. This is surprising as

silicone oil has been used successfully for the removal of VOCs in several previous studies [9–12]. Chiang et al. [9] and Majumdar et al. [11] did not specify which specific silicone oil was used, but both Darracq et al. [10] and Heymes et al. [12] used polydimethylsiloxane (PDMS). The average molecular weight of PDMS is twice that of the silicone oil used in this study, which could explain the difference in solubility. Due to the poor solubility of wood tar and sludge in the silicone oil, no further experiments were carried out using this oil in the present study.

#### 3.2 Composition of sludge

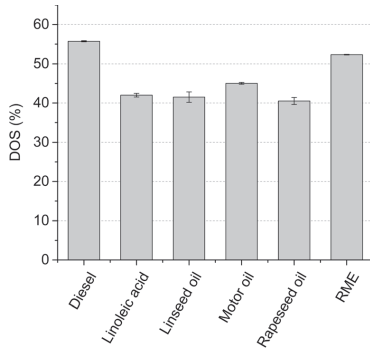
Due to the complexity of the sludge, it was only possible to obtain a rough estimate of the composition. The analysis showed that the sample consists of 25 wt% solids, 27–35 wt% water and tar compounds with a boiling point below 110 °C and 3 wt% of tar compounds detected with the analysis method described in Section 2.3.5. It should be noted that a small amount of the heavier tars will have been vaporized at 110 °C depending on their vapour pressure, but they are not fully removed. The remaining weight fraction is assumed to consist of RME and heavy tars, but due to the complexity of the sample, it was not possible to determine the exact composition of this fraction.

#### 3.3 Samples

The centrifuged samples consisted of three distinguishable phases: Phase 1, the upper liquid phase consisting of scrubber liquid and lighter tars dissolved in the scrubber liquid; Phase 2, an intermediate phase that was a mixture of the liquid top phase and solid bottom phase; and Phase 3, the solid bottom phase, consisting of heavy insoluble tars, ash and water. The ratio between the phases varied between the centrifuged samples, and this made it possible to divide the samples into three categories, as illustrated in Fig. 1. Category C samples are the most desirable as they contain only two distinguishable phases and a liquid upper phase free from particles.

#### 3.4 Separation

The separation of the liquid phases improved, i.e. changed from Category A to Category C, with increased centrifugation time and higher temperature. Figure 2 shows the performance of the scrubber liquids for the combination of the highest temperature and longest time (condition IX). Bearing in mind the definition of DOS, and taking the fact that the samples consisted of 50 wt% scrubber liquid into account, upper phase DOS values below 50 % are the direct effect of scrubber liquid being trapped in the lower phase. In an industrial system, this would mean a continuous loss of scrubber liquid with the rejected sludge. For this reason, the most desirable results



**Fig. 2** The DOS of the scrubber liquids following centrifugation at 90 °C for 10 min (IX in Table 2)

are those where the DOS is as close to 50 % as possible. As can be seen in Fig. 2, the best separation efficiency was obtained with diesel and RME.

Category C samples were obtained for diesel for conditions II–IX, for linoleic acid (IX) and RME (III, VI, VIII and IX), see Table 4. All other scrubber liquids contained a substantial amount of Phase 2 at all parameter combinations. This is further illustrated by the results for scrubber liquid recovery, also given in Table 4. Category C samples with recoveries exceeding 100 % (RME III, VI and IX and diesel II, III, V, VI, VIII and IX) can be explained by wood tar, together with possible scrubber liquid residue previously trapped in the sludge, being added to Phase 1. All other values exceeding 100 % are the result of the inability to clearly separate Phases 1 and 2 when performing the weighing, leading to the inclusion of solid particles in the upper, liquid phase.

Based on the DOS and the data presented in Table 4, it is possible to rank the scrubber liquids studied in terms of their

separation efficiency and thus their suitability for recovery in a centrifugation-based recovery system. The proposed ranking from most to least suitable is:

diesel > RME > linoleic acid > linseed oil > rapeseed oil > motor oil

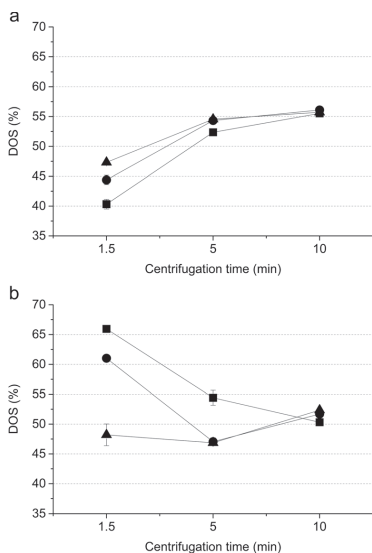
Due to the superiority of diesel and RME, only these two scrubber liquids were selected for further investigation. Figure 3 shows the DOS for the diesel (a) and RME (b) samples.

It can be seen in Fig. 3a that the separation efficiency for diesel increases with increased centrifugation time and sample temperature. However, the same behaviour is not seen for RME (Fig. 3b) where the DOS decreases with centrifugation time. This can be explained by the fact that under conditions I, II, IV, V and VII, RME falls into Category B. These samples contain solid particles in the upper phase, which increases the DOS. The effect of temperature is more prominent at the shortest centrifugation time of 1.5 min, in both Fig. 3a, b. This is most likely the consequence of the lack of heating inside the centrifuge, and the rapid fall in temperature to 30 °C. Due to this fall in temperature, it is not possible to determine whether the temperature affects the separation efficiency at longer centrifugation times. The temperature effects needs further investigation in order to draw any conclusions, however, the issue could not be studied further due to the constraints in the experimental setup.

Based on the same reasoning as for the scrubber liquid recovery, a DOS for Category C samples below 50 % indicates that scrubber liquid is trapped in the bottom phase, and values above 50 % are the result of wood tar in the upper phase. Translating these results into an industrial centrifugation recovery system, taking into account the difficulty of operating at a constant DOS of 50 %, there would either be a loss of scrubber liquid via the sludge, or an increase in scrubber liquid volume due to lighter tar components. Also,

**Table 4** Scrubber liquid recovery and sample category for the scrubber liquids and all parameter configurations

Scrubber liquid		Parameter combination								
		I	II	III	IV	V	VI	VII	VIII	IX
Diesel	Category	B	C	C	C	C	C	C	C	C
	Recovery (%)	81	105	111	89	108	112	94	109	111
Linoleic acid	Category	A	A	B	A	B	B	B	B	C
	Recovery (%)	140	122	100	127	108	88	119	106	84
Linseed oil	Category	A	A	B	A	A	B	A	B	B
	Recovery (%)	120	109	101	129	106	91	124	103	83
Motor oil	Category	A	A	A	A	A	A	A	A	B
	Recovery (%)	146	134	119	137	125	97	118	102	88
Rapeseed oil	Category	A	A	A	A	A	B	A	B	B
	Recovery (%)	125	112	94	130	107	91	120	98	81
RME	Category	B	B	C	B	B	C	B	C	C
	Recovery (%)	132	109	101	122	94	103	96	93	104

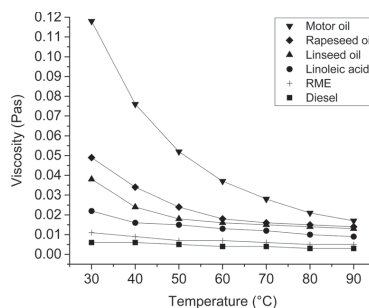


**Fig. 3** The DOS for diesel (a) and RME (b) as a function of centrifugation time and temperature, 50 °C (■), 70 °C (●), 90 °C (▲)

a separation efficiency corresponding to Category C samples may not be achievable, depending on the efficiency of the centrifuge and its operating conditions, thus resulting in scrubber liquid containing solid particles being recirculated to the scrubber system.

### 3.5 Viscosity measurements

As discussed above, the separation efficiency varies significantly depending on the scrubber liquid, but the temperature can also affect the degree of separation, although this can only be seen for centrifugation time of 1.5 min. Viscosity measurements were performed on all the fresh scrubber liquids to determine whether the observed difference in separation efficiency could be explained by the viscosity of the scrubber liquid, and also if the effect of temperature on the separation could be correlated to a temperature-dependent change in the viscosity. As can be seen in Fig. 4, the viscosity of the scrubber liquids, with the exception of motor oil, remained relatively constant over the temperature range investigated. This implies that the effect of temperature on the separation efficiency is not correlated to the viscosity of the scrubber liquid. The increase in separation efficiency can instead be explained by an increase in the rate of diffusion and solubility. There is, however, an apparent correlation between the separation efficiency and the viscosity of the different scrubber liquids as Category C samples were only obtained for scrubber liquids



**Fig. 4** Viscosity as a function of temperature for the scrubber liquids studied

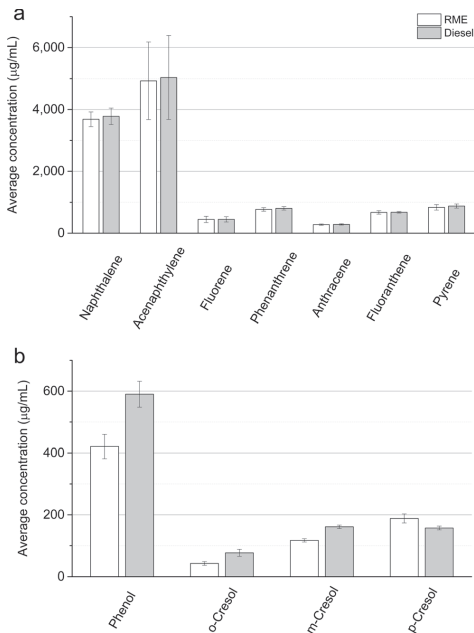
with a viscosity lower than 0.01 Pas. The separation efficiency increases with decreasing scrubber liquid viscosity. This observation corresponds well with the ranking of the scrubber liquids given in Section 3.4 above.

### 3.6 Analysis of tars

The analysis of dissolved tars was only performed for the diesel and the RME samples. The analysis of the upper phases showed no clear correlation between the amount of dissolved tar components and the parameter combination. The average tar component concentrations for all RME and diesel parameter combination are presented in Fig. 5a (aromatic tar components) and b (phenolic tar components).

Neither fresh diesel nor fresh RME contained any of the tar compounds found in the spent liquids (data not shown). This means that the tar dissolved in the spent scrubber liquids originates from either the wood tar or the sludge. As can be seen in Fig. 5, the dissolution of both aromatic and phenolic tar components is slightly higher in diesel than in RME, but the difference is small. In addition to the compounds included in Fig. 5, small amounts of other 4- and 5-ring PAHs were also present. The average concentration of benzo(a)pyrene was  $121 \pm 22$   $\mu\text{g/mL}$  in diesel and  $127 \pm 19$   $\mu\text{g/mL}$  in RME. Benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene and chrysene were detected, but were not quantified due to interference from unknown aromatic compounds. Variations in the results are believed to be the effect of measurement precision and not actual variations in tar concentration. The measurement error for both the gas chromatography and the HPLC-UV-DAD system was estimated to be  $\pm 10\%$ . The values for all compounds except acenaphthylene, benzo(a)pyrene and o-cresol lie within this interval. The high error for these compounds may be due to interference from other compounds, as in the case of the 4- and 5-ring PAHs.

The two major tar compounds found in the analysis is naphthalene and acenaphthylene. These are considered to be light tars which are fully soluble in the scrubber medium and



**Fig. 5** Average concentrations of aromatic tar components (a) and phenolic tar components (b)

they will therefore not be separated in the centrifuge. Instead these compounds will precipitate when the concentration in the scrubber liquid increases. This issue will have to be addressed in a system perspective either by removal of the light tars or by replacing part of the scrubber medium.

#### 4 Conclusions

The above results show that it is only possible to remove insoluble tars by centrifugation, and soluble tars will be recirculated together with the scrubber liquid. It is difficult to predict how this accumulation will affect the efficiency of the scrubber without performing long-term experiments. If the dissolved tars prove to be a problem, causing a decrease in scrubber efficiency and thus the quality of the producer gas with time, it might suffice to bleed off a fraction of the saturated scrubber liquid and replace it with fresh scrubber liquid. Otherwise, it might be necessary to add additional regeneration equipment, i.e. a stripper, to remove dissolved tars from all or a fraction of the scrubber liquid. If this proves to be the case, it could be argued that the efficiency of centrifugation for scrubber liquid regeneration is inadequate.

The experiments in this study have been executed in a controlled laboratory environment. To obtain results that are more realistic, centrifugation experiments must be performed on a larger scale, preferably in a real biomass gasification plant that uses a scrubber for gas cleaning. This will provide an opportunity to study the long-term effects, i.e. the effects of the accumulation of tars in the scrubber liquid on the scrubber efficiency and the quality of the producer gas. Also, techno-economic studies should be performed to evaluate how adding a centrifuge for scrubber liquid regeneration affects the overall process economy.

The scrubber liquids studied here can be ranked with regard to their suitability for cleaning in a centrifugation-based recovery system as follows: diesel > RME > linoleic acid > linseed oil > rapeseed oil > motor oil. The separation efficiency is highly dependent on the viscosity of the scrubber liquid, the centrifugation time and the temperature. Centrifugation appears to be a promising method for the regeneration of spent scrubber liquid, but long-term effects must be studied before drawing a general conclusion.

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Paper V





# Catalytic Abatement of $\text{NH}_3$ Using $\text{NO}_x$ in Reducing Environment

Laura Malek<sup>1</sup> · Per Tunå<sup>1</sup> · Christian Hulteberg<sup>1</sup>

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**Abstract** Removal of ammonia from synthesis gas is an important step in gas purification to prevent poisoning of downstream catalyst or formation of nitrogen oxides on combustion. This publication proposes that ammonia can be removed by using selective catalytic abatement with  $\text{NO}_x$ , not unlike the selective catalytic reduction of  $\text{NO}_x$  but under reducing environment. Two different catalysts have been used for the experiments;  $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$  and H-mordenite. The conducted experiments were performed on a model synthesis gas and served to investigate the selectivity and to some extent the longevity of these catalysts under reducing atmosphere, and also the effect of water on the catalyst performance. A number of catalyst characterisation methods have been used to obtain a better understanding of the catalyst morphology and surface. The methods that have been used are Raman spectroscopy, Brunauer–Emmett–Teller nitrogen adsorption, X-ray diffraction and temperature programmed desorption using ammonia. The initial performance with respect to conversion and selectivity is good for the vanadia-based catalyst, but it is not chemically stable. This is manifested by a change in the catalyst crystal structure suggesting an oxygen depletion of the titania support and decreased activity with time-on-stream. The mordenite catalyst is stable but the activity and selectivity, especially to avoid the formation of  $\text{N}_2\text{O}$ , needs to be improved before implementation. Based on the experimental work performed, none of the catalysts in their present state are suitable for the proposed operating conditions.

**Keywords** Selective catalytic reduction ·  $\text{NO}_x$  ·  $\text{NH}_3$  · H-mordenite · Vanadium · Catalysts

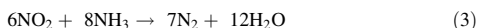
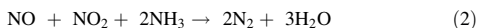
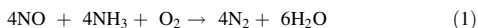
## 1 Introduction

Due to increasing concerns for greenhouse gas emissions, there has been an increase in the use and interest for using biomass. One of the areas that are considered for the use of biomass is gasification for the generation of synthesis gas [1, 2]. The thus generated gas can be used in multiple applications such as fuel synthesis [2–4], chemical synthesis [5] and heat and power production [6, 7]. There are a number of interesting aspects of gasification; one is the production of the gas in the gasifier, including operating conditions and equipment design, and another is downstream gas purification. This paper is focusing on the second aspect and in particular the removal of ammonia in the synthesis gas.

A typical synthesis gas exiting a gasifier will contain between 1000 and 5000 ppm of ammonia [6, 8]. Depending on the downstream processing, there will be different amounts of ammonia still in the gas prior to gas utilisation; reforming of the hydrocarbons and tars will for instance lower the concentration substantially. The ammonia stem from the nitrogen content of the wood and will have to be removed from the synthesis gas in one way or the other as it may either poison catalysts downstream the gasifier or form nitrous oxides ( $\text{NO}_x$ ) on combustion [9, 10]. The thus formed  $\text{NO}_x$  will contribute to acid rain and smog if not cleaned up properly. The clean-up is traditionally performed using selective catalytic reduction (SCR) of the  $\text{NO}_x$  by injection of ammonia/urea [11–19]. The reactions involved are described by reaction formulas (1–3).

✉ Christian Hulteberg  
christian.hulteberg@chemeng.lth.se

<sup>1</sup> Department of Chemical Engineering, Lund University,  
Box 124, 221 00 Lund, Sweden



The ammonia may of course be removed by water scrubbing as it is very soluble in acid or neutral water. This however requires the gas to be cooled and the ammonia/water solution will have to be purified by other means. There are publications on the removal of ammonia by selective catalytic oxidation with air or oxygen (e.g., [20]), however the oxygen-rich environment of these publications make them less relevant to the synthesis gas case discussed here. In addition, there are a few publications where the selective oxidation has been performed under reducing environment. These publications have either to low concentrations of  $\text{H}_2$  and  $\text{CO}$  to be relevant [21, 22] or operate with large enough temperature increase to make cracking of ammonia plausible [23–26] and the catalytic effect questionable.

In an earlier publication by Tunå and Brandin [27] the removal of ammonia using selective catalytic abatement with  $\text{NO}_x$  was investigated. The desired reactions are the same as for the traditional SCR of  $\text{NO}_x$ , but under reducing atmosphere. The study was performed with a gas composition close to an expected environment downstream a gasifier. The investigation provided a proof-of-concept using both injection of gaseous  $\text{NO}_2$  and nitric acid. In the study, two catalyst were studied, a  $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$  and a H-mordenite. The two catalyst systems chosen,  $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$  and a H-mordenite, are both well known to promote the SCR reaction [12]. The investigated catalysts are however different in composition and operate in different temperature ranges with H-mordenite being active and selective in a higher temperature window than the vanadia-based catalyst. The same catalysts,  $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$  and H-mordenite, have been used in this study. The initial results were promising, but there were several aspects left to investigate further. This paper is intended to shed further light on these aspects. The first aspect is the question of selectivity of these catalysts under reducing atmosphere. The second aspect is the longevity of the catalysts in this environment. The third aspect is the effect of water on the catalyst performance, a factor known to lower activity of SCR catalysts under oxidising conditions [28–30]. These questions have been answered by a combination of further experimental work and catalyst characterisation for reaction (3).

## 2 Experimental

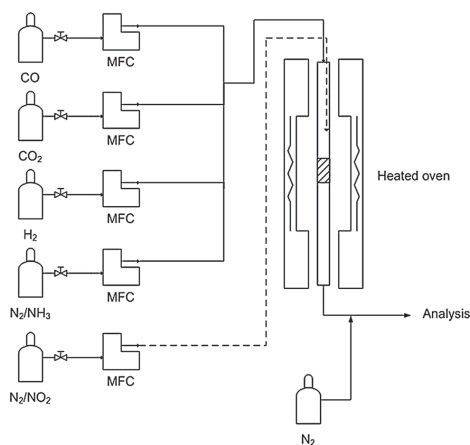
### 2.1 Catalyst Testing

Two different catalysts have been used for the experiments;  $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$  and H-mordenite. Both are used as SCR

catalyst in the industry today but they differ in chemical composition, structure and optimal operating temperature. These factors can result in different resistance towards the reducing environment. The H-mordenite has a Si/Al ratio of 21 and is manufactured by Zeolysts. The vanadium catalyst is used commercially and is produced by BASF.

The catalysts were operated at different temperatures. The SCR experiments were conducted at temperatures in-between 563–723 K when using the H-mordenite catalyst and in-between 573–673 K when using the vanadium catalyst. Both catalysts had a particle size of 200–400  $\mu\text{m}$ . A schematic illustration of the experimental setup can be seen in Fig. 1. After performing the experimental runs, the catalysts were operated an additional 24 h on 723 K in the mordenite case and 673 K in the vanadium catalyst case yielding an overall time-on-stream of circa 100 h. The model producer gas used in the experiment consisted of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$  and a mixture of 0.5 vol % ammonia in  $\text{N}_2$ , see Table 1 for compositions. The experiments were performed both with and without the addition of steam to investigate how water affected the performance of the catalyst. In the cases when the effects of steam were studied, the steam was added to the gas stream in the form of water provided by a syringe pump set to a constant feeding rate. The syringe content was enough to sustain constant water feed rate for 6 h. The gas/water mixture was heated to over 373 K before entering the reactor to ensure that no liquid water was present.  $\text{NO}_2$  was added separately via a steel tube inside the reactor, approximately 40 mm above the catalyst bed.

These gas flows corresponds to a gas hourly space velocity of 225,000 and 250,000  $\text{h}^{-1}$  respectively through



**Fig. 1** Experimental setup

**Table 1** Gas composition for dry and wet SCR experiments

Compound	Dry		Wet	
	ml/min	vol %	0.75	0.25
NH <sub>3</sub>	0.75	0.28	0.75	0.25
NO <sub>2</sub>	0.75	0.28	33.75	11.25
CO	33.75	12.68	33.75	11.25
CO <sub>2</sub>	33.75	12.68	33.75	11.25
H <sub>2</sub>	33.75	12.68	33.75	11.25
N <sub>2</sub>	163.5	61.40	163.5	54.5
Sum	266.25	100	300	100

the catalytic bed. The used reactor consists of a glass tube placed inside an electrical oven. The glass tube is 4 mm in diameter and has sintered glass in the middle to support the catalytic bed. A thermocouple was placed inside the glass tube and measured the reaction temperature just above the catalytic bed.

Exiting gas was diluted with N<sub>2</sub> before proceeding to analysis where ammonia, water, NO, NO<sub>x</sub> and N<sub>2</sub>O content were measured. Ammonia and water content was measured with a Sick GME700 Laser Gas Analyser. The GME700 uses direct laser spectroscopy and has a measuring range of 0–5000 ppm for ammonia and 0–3000 ppm for water. NO and total NO<sub>x</sub> content was measured with an ECO PHYSICS CLD 700 RE ht via chemiluminescence. The instrument has four measuring ranges from 0–10 ppm to 0–10,000 ppm with a minimal detectable concentration of 0.1 ppm. N<sub>2</sub>O content was measured with a SICKIMAI-HAK Sidor gas analyser. It measures N<sub>2</sub>O within the range of 0–100 ppm using non-dispersive infrared spectroscopy. To avoid condensation of water or formation of ammonium nitrate before the measuring equipment the gas was transported through tubing that was heated to 453 K.

The experiments were carried out by starting all gas flows, except that of NO<sub>2</sub>, and allow the system to reach steady-state at the desired reaction temperature. Steady-state was reached when the catalyst was fully saturated with ammonia. The reason why the catalyst was saturated with ammonia before the addition of NO<sub>2</sub> was to ensure that changes in ammonia concentration during the experiment are due to the reaction with NO<sub>2</sub> and not to the adsorption of ammonia on the catalyst. When steady-state was reached the NO<sub>2</sub> was added and the changes in ammonia, NO, NO<sub>x</sub> and N<sub>2</sub>O concentration was monitored until the system reached a second steady-state, when the measured ammonia concentration had stabilized. The selectivity towards NO, N<sub>2</sub>O and N<sub>2</sub> was calculated according to Eqs. 1–3.

$$S_{NO} = \frac{C_{NO}}{(C_{NH_3,in} \cdot X_{NH_3})} \quad (1)$$

$$S_{N_2O} = \frac{C_{N_2O}}{(C_{NH_3,in} \cdot X_{NH_3})} \quad (2)$$

$$S_{N_2} = 1 - (S_{NO} + S_{N_2O}) \quad (3)$$

## 2.2 Catalyst Characterization

A number of catalyst characterisation methods have been used to obtain a better understanding of the catalyst morphology and surface. The methods that have been used are Raman spectroscopy, Brunauer–Emmett–Teller (BET) adsorption, X-ray diffraction and temperature programmed desorption (TPD) using ammonia. Both catalysts were analysed both before (termed fresh) and after the experiments (termed used). All materials were analysed for changes in their BET surface areas measured by the adsorption of nitrogen at liquid nitrogen temperature using a Micromeritics ASAP 2400 instrument after degassing for 16 h at 623 K. Pore volume analysis was performed using the BJH method [31]. The Halsey formula [32] was used to calculate the thickness of the adsorbed layer (*t* value). The desorption-isotherm was used for the analysis; the values are average values of 2 analysis runs.

Fourier transform (FT)-Raman spectra were recorded on a Bruker IFS 66 FT-IR spectrometer equipped with the Bruker FRA 106 FT-Raman add-on. A low-power, diode-pumped Nd:YAG laser, model DPY 301 (1064 nm) from Adlas, and a liquid-nitrogen-cooled, high-sensitivity model 403 germanium diode detector from Applied Detector Corp. were used. The laser power was 100 mW and the resolution was 4 cm<sup>-1</sup>. For every spectrum, 1000 scans were averaged. Powder X-ray diffractograms (XRD) were collected with a Seifert C3300 TT diffractometer, using nickel-filtered CuK<sub>α</sub> radiation for both fresh and used samples. In the measurements, ground sample was used and the sample was supported on a rotating sample holder.

The catalyst acidity was measured for all of the investigated catalysts using ammonia-TPD on a Micromeritics 2900. The catalyst sample was inserted into a glass tube and degassed at 673 K for 1 h in helium atmosphere. After degassing the temperature was lowered to 323 K and the catalysts were saturated with ammonia using a gas mixture of 5 % NH<sub>3</sub> in He. Physisorbed ammonia was desorbed at 323 K by switching back to He before the temperature ramp was started. The temperature ramp was set to 873 K with 10°/min ramp-rate.

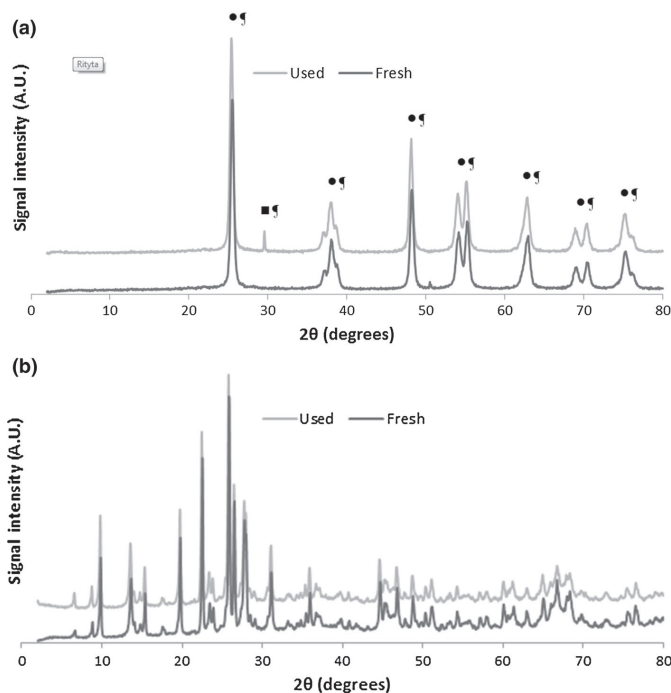
## 3 Results and Discussion

### 3.1 Catalyst Characterization

The surface analysis of the catalyst using nitrogen adsorption at liquid nitrogen temperature shows that there

**Table 2** The results of the nitrogen adsorption measurements

	BET surface area (m <sup>2</sup> /g)	Pore volume (ml/g)	Average pore diameter (nm)
V <sub>2</sub> O <sub>5</sub> /WO <sub>3</sub> /TiO <sub>2</sub>			
Fresh	61.0	0.26	17.29
Used	64.1	0.26	16.25
H-mordenite			
Fresh	406.6	0.33	3.37
Used	360.6	0.33	3.61

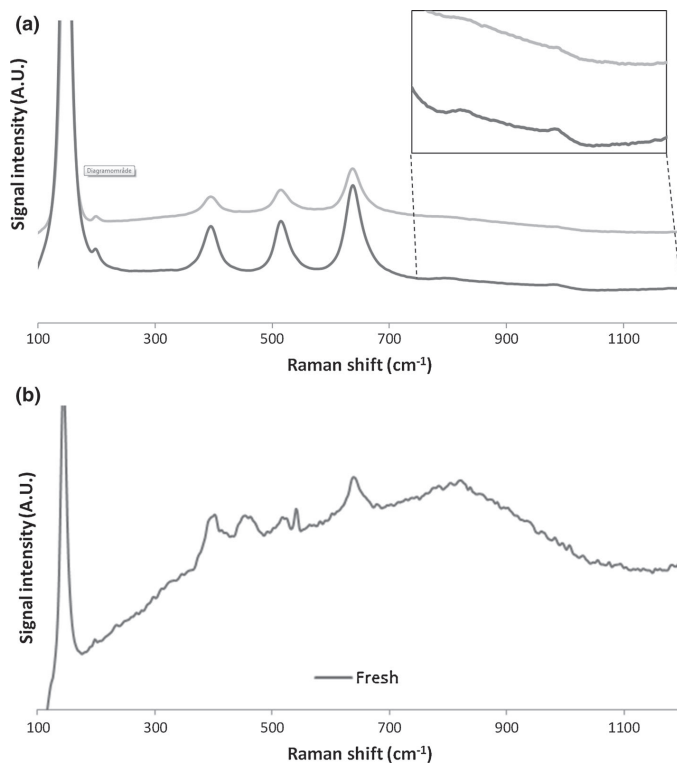
**Fig. 2** **a** XRD diffractogram for fresh and used V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub>. *filled circle* denote anatase and *filled square* reduced TiO<sub>x</sub>-species. **b** XRD diffractogram for fresh and used H-mordenite

is a small surface increase in the case of the vanadium-based catalyst, Table 2. The increase is some 5 % and may perhaps be attributed to unblocking of pores during rearranging of tungsta and/or vanadia on the surface. This behaviour is not common to this type of catalysts [33] during operation and is most likely due to the reducing environment. The mordenite catalyst shows a more expected behaviour with a decrease in surface area by some 10 %.

X-ray diffractograms were collected for both catalysts before and after use and are depicted in Fig. 2a and b. The peaks in Fig. 2a are consistent with the anatase-phase of

the titania identified also by other researchers [34, 35]. There is however a peak at  $2\theta$  about  $29^\circ$  that appears with treatment in the reducing environment. This peak is most likely attributed to reduced titania. Indeed, there are several reduced titanium oxides (Ti<sub>4</sub>O<sub>7</sub>, Ti<sub>7</sub>O<sub>13</sub>, Ti<sub>8</sub>O<sub>15</sub>) showing peaks in this area. Also the reduced form (H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>) display peaks at  $2\theta$  about  $29^\circ$ , with the rest of the peaks covered by the anatase phase [36]. This reduced titania represents a significant change in the catalyst bulk composition before and after testing. The diffractogram in the case of the mordenite is consistent with the material and shows no change over the testing period.

**Fig. 3** **a** Raman spectra for fresh and used  $V_2O_5/WO_3/TiO_2$   
**b** Raman spectra for fresh H-mordenite



The Raman shift is reported in Fig. 3a and b for the two catalysts. The Raman shift of the vanadia-based catalyst is consistent with other investigators results with an intense peak at  $120\text{--}140\text{ cm}^{-1}$ , two peaks at  $390\text{--}400$  and  $510\text{--}530\text{ cm}^{-1}$  and a slightly higher peak at  $630\text{--}640\text{ cm}^{-1}$  which are all assigned to the anatase  $TiO_2$  phase [37, 38]. If the  $700\text{--}1200\text{ cm}^{-1}$  section is investigated in more detail, there is a band at about  $800\text{ cm}^{-1}$  which reveals crystalline  $WO_3$  and is attributed to  $W\text{--}O\text{--}W$  bonds. The unresolved shoulder at  $970\text{--}990\text{ cm}^{-1}$  indicate  $W = O$  terminal bonds [39, 40]. There is little change to the position of the anatase peaks ( $390\text{--}400$ ,  $510\text{--}530$  and  $640\text{--}640\text{ cm}^{-1}$ ) over the testing period of 100 h. The bonds allocated to the tungsta ( $800$  and  $980\text{ cm}^{-1}$ ) are much less pronounced after operation on stream. There are no peaks assigned to vanadia in the Raman spectra as it has been shown that under the influence of water on the catalyst surface, the monomeric vanadyl-specie peak normally seen at  $1030\text{ cm}^{-1}$  shift to lower wavenumber and a band at  $990\text{ cm}^{-1}$  grows stronger [39]. This band is overlapped

with the terminal  $W = O$  band already discussed earlier in the text.

Mordenite is of the structural group 5–1 and is built up by five-membered tetrahedron rings and an additional interstitial single tetrahedron. The mordenite Raman shift before use display peaks at about  $400$ ,  $450$ ,  $470\text{ cm}^{-1}$ , which is consistent with other findings in literature [41, 42]. The bands at  $400$  and  $470\text{ cm}^{-1}$  are attributed to the  $\nu_s$  modes of structures five membered rings (cmcm space group). There is also a band at about  $800\text{--}850\text{ cm}^{-1}$  that is attributed to silicon non-bonded oxygen whilst the band at  $950\text{--}1250\text{ cm}^{-1}$  is explained by the zeolite-Si-O-Al asymmetric stretching [42]. The peak at about  $640\text{ cm}^{-1}$  is not explained by the mordenite structure per se and can perhaps be assigned to the Al-O vibration. Both the vanadia and the mordenite catalysts display a much higher signal-ton-noise ratio after operation. This is displayed by the higher base-line in the vanadia case and in the mordenite case, no information was possible to discern and the result is not depicted. This phenomenon is much discussed



and usually attributed to simple organic molecules turning into fluorescent species at high temperatures or iron present in the samples [43]. The most likely explanation in this instance is the formation of fluorescent species from the carbon-containing molecules in the gas.

The acidity of the catalysts has been investigated using ammonia-TPD, Table 3. In the case of the vanadia catalyst, the curve for the fresh sample showed two peaks, one large with a maximum at 389 K and a smaller one with a maximum at 702 K, where the second peak may be attributed to the titania [44]. The desorbed amount changes over time such that the used catalyst adsorbs about 21 % less ammonia than the fresh one. It is also interesting to note that the acidic strength of the sites left is reduced (evidenced by the decrease in the first peak maximum temperature) and that the second peak disappears. The mordenite catalyst shows a different behaviour. The used sample adsorbs about 16 % more ammonia than the fresh sample. However, the acidic strength of the sites is reduced as evidenced by the downward shift in the first maximum peak temperature by almost 50 K. There is also a slight

increase in the second maximum peak temperature, albeit smaller than for the first peak. Comparing the absolute values, the two used catalysts adsorb about the same amount of ammonia, even though there is quite a significant difference in the two fresh catalysts.

### 3.2 Reduction of Ammonia

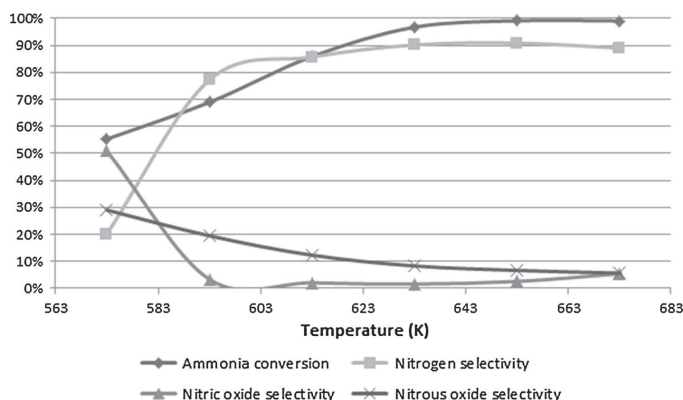
Results from the  $V_2O_5/WO_3/TiO_2$  experiments, with and without the addition of water in the model gas, can be seen in Figs. 4 and 5. The conversion of  $NH_3$  increases with increasing temperature in both cases, although the overall conversion is slightly lower (over the entire temperature span) in the added water case compared to the case without water. In the case without water (Fig. 4) there is a clear shift from formation of  $NO$  towards  $N_2$  when increasing the reaction temperature from 573 to 593 K. The selectivity to  $NO$  has a minimum close to 600 K and increases slightly with increasing temperature while the selectivity to  $N_2O$  shows a steady decrease. Both the conversion of  $NH_3$  (99 %) and the selectivity towards  $N_2$  (91 %) reaches a maximum at 653 K.

Selectivity towards  $N_2$  is greater for the case with added water as can be seen in Fig. 5. This is true for the entire temperature range, but especially true for lower reaction temperatures where  $N_2$  selectivity is 60 percentage points greater compared to the case without water. The addition of water favours  $N_2$  production while suppressing the production of  $NO$  and  $N_2O$ . As in the case with added water, the maxima for  $NH_3$  conversion (97 %) and  $N_2$  selectivity (94 %) are located at 653 K; the conversion of  $NH_3$  is reduced by a few percentage points over the entire temperature range on the addition of water which is in-line with the performance of the catalyst under oxidising conditions [45].

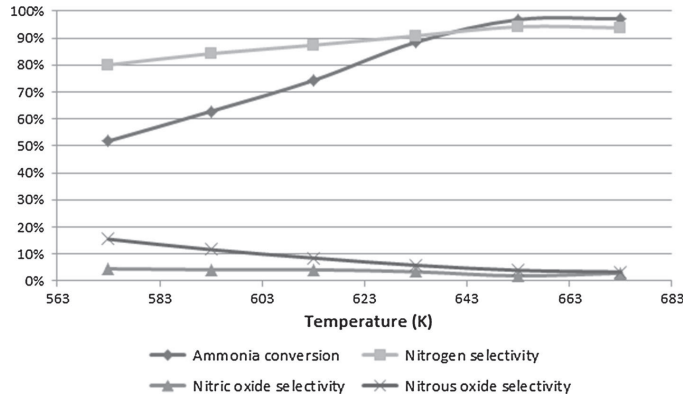
**Table 3** The results of the temperature programmed desorption experiments

	Desorbed ammonia ( $\mu\text{mol}/\text{m}^2$ )	Tmax1 (K)	Tmax2 (K)
$V_2O_5/WO_3/TiO_2$			
Fresh	6.69	389	702
Used	5.28	369	–
H-mordenite			
Fresh	4.55	466	819
Used	5.53	408	830

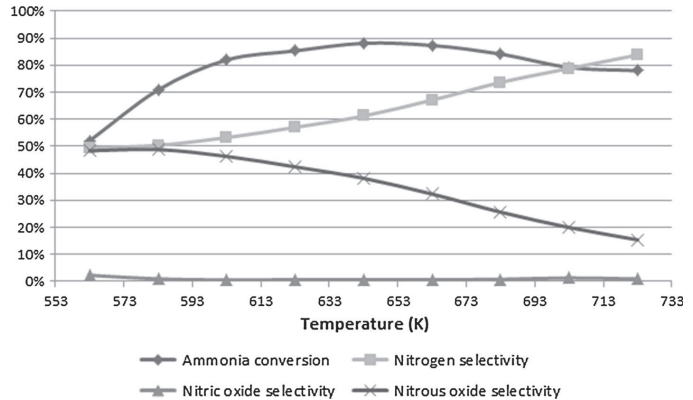
**Fig. 4** Ammonia conversion and selectivity results for  $V_2O_5/WO_3/TiO_2$  without water



**Fig. 5** Ammonia conversion and selectivity results for  $V_2O_5/WO_3/TiO_2$  with water



**Fig. 6** Ammonia conversion and selectivity results for H-mordenite without water



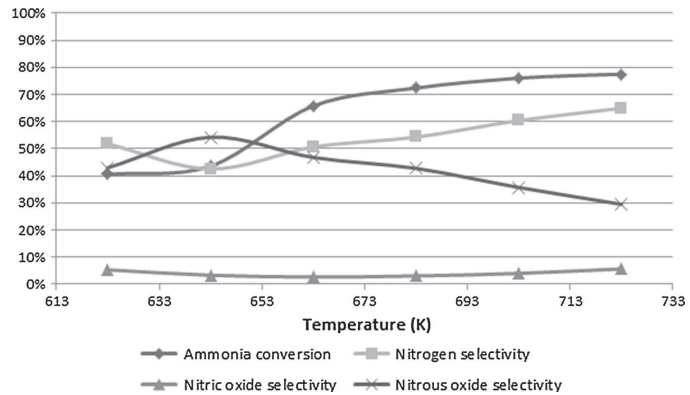
Long-term experiments (100 h) showed a decrease in conversion with about 10 % over the operational period.

Results from the H-mordenite experiments, both with and without the addition of water in the model gas, can be seen in Figs. 6 and 7. Unlike the  $V_2O_5/WO_3/TiO_2$  experiments, the H-mordenite cases differ significantly in preferred reaction temperature. In the case without water, Fig. 6, the catalyst operates at a much lower temperature and reaches higher  $NH_3$  conversion and  $N_2$  selectivity compared to the case with added water, Fig. 7. Also the selectivity towards NO and  $N_2O$  is greater overall in the case with added water compared to the case without.  $NH_3$  conversion reaches a maximum of 88 % at 643 K for the case without added water before decreasing with increasing temperature.  $N_2$  selectivity

increases steadily while the selectivity for NO decreases with increased temperature. The  $N_2O$  selectivity does not vary significantly, it is however much higher than what can be seen under oxidising conditions [46].

As mentioned, H-mordenite experiments conducted with the addition of water to the model gas require a much higher reaction temperature to achieve the same level of  $NH_3$  conversion compared to the case without added water. This indicates a competitive adsorption of water and  $NH_3$ . Both  $NH_3$  conversion and  $N_2$  selectivity increases while the  $N_2O$  selectivity decreases with increasing temperature. No major long-term effects were observed with respect to conversion or selectivity over the 100 h operational period.

**Fig. 7** Ammonia conversion and selectivity results for H-mordenite with water



#### 4 Conclusions

It can be concluded from the presented work that under the investigated conditions the vanadium-based catalyst is more suitable for  $\text{NH}_3$  removal based on the initial performance. The catalyst outperforms the mordenite catalyst by about 10 and 20 percentage points with respect to conversion at the best operating conditions for respective catalyst under dry and wet conditions respectively. The largest difference however is the selectivity to  $\text{N}_2\text{O}$  which is much lower in the case of the vanadium-based catalyst. It is also an interesting observation that the selectivity towards  $\text{N}_2$  is further improved by the addition of water to the gas mixture in the case of vanadium-based catalyst. However for the mordenite catalyst, the selectivity is not favoured by the addition of water and the activity is instead lowered significantly with steam present.

The vanadium catalyst is significantly changed as even the crystal structure as detected by XRD is changed. The reduction of the titanium dioxide into a more oxygen depleted system is a major difference compared to the operation under oxidising environment. There is also a significant change in the strength and amount of acid sites as evidenced by the second peak in the ammonia desorption experiments disappearing and the first peak shifting towards lower temperatures. This indicates that the catalyst is not physically stable under the present conditions. The catalyst performance also worsened during the long-term operation indicating a long term effect. The mordenite catalyst was less affected by the operating conditions. There was a small reduction of the BET surface area, which was not unexpected. Indeed there was also an increase in the amount of acid sites on the catalyst. Due to the performance of the catalyst in this study, it is believed that this catalyst may be stable in the environment.

However, to make this a commercially viable alternative, the selectivity to nitrogen will have to be increased.

There is however still some things to sort before commercialising the technology, selectivity aside. The synthesis gas will not only contain ammonia, but also sulphur. The sulphur will be in the form of  $\text{H}_2\text{S}$ , COS and  $\text{CS}_2$  with hydrogen sulphide being the main component [6, 8]. Normally, SCR catalysts are positively influenced by sulphur, but this is in the form of sulphur oxides [47]. It will be interesting to evaluate the catalysts performance under sulphur-laden operation.

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Department of Chemical Engineering  
Faculty of Engineering, LTH  
Lund University

