ECN
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SenterNovem

Gas cleaning
downstream biomass gasification

Status Report 2009

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Abstract

The government wants to help realize an affordable, reliable and clean energy economy, while fully acknowledging the role the market ought to play in this development. The role of the Energy Research Subsidy (in Dutch abbreviated as EOS) programme is to initiate and support the necessary innovation processes. The biomass research has been divided into three main areas, being *(i)* biorefining, *(ii)* electricity and heating, and *(iii)* gasification, gas cleaning, conditioning and syngas production. While the EOS programme can thus offer support at each of the stages of the energy innovation trajectory, it also helps the supply of knowledge to better meet the demand of the market. In order to stimulate the supply of knowledge status reports are published by relevant stakeholders upon request from the Dutch Agency for Innovation and Sustainability (SenterNovem). The status report on gas cleaning focuses on cleaning technologies downstream biomass gasifiers to manufacture clean gas, from which electricity and heat, transport fuels, chemicals and 'new gases' (such as SNG and hydrogen) can be produced efficiently. It provides an overview of the current status, the key players, the motives and challenges, and the ongoing remaining R&D. Although upgrading of biogas or landfill gas is not considered to be a R&D topic within the EOS research area "gasification, gas cleaning, conditioning and syngas production", the status report at hand also provides information focused at these existing upgrading technologies. The technologies in this sector may also apply for gas obtained from thermo-chemical conversion processes.

Samenvatting

Het ministerie van Economische Zaken heeft beleid ontwikkeld dat gericht is op het realiseren van een betaalbare, betrouwbare en schone energievoorziening. Een van de programma's die invulling geven aan dit beleid is Energie Onderzoek Subsidie (EOS). Het programma Energie Onderzoek Subsidie (EOS) heeft tot taak de benodigde innovatieprocessen op gang te brengen en te ondersteunen. Het aandachtsgebied Biomassa wordt opgedeeld in drie onderzoeksterreinen, te weten *(i)* bioraffinage, *(ii)* elektriciteit en warmte, en *(iii)* vergassing, gasreiniging, conditionering en syngasproductie. Het EOS-programma biedt ondersteuning in elk van de fasen van het energie-innovatie traject en stimuleert de noodzakelijke kennis dissiminatie. Ter stimulering van kennis dissiminatie worden door relevante belanghebbenden op verzoek van het Nederlandse agentschap voor duurzaamheid en innovate (SenterNovem) status rapporten gepubliceerd. Het status rapport over gasreiniging richt zich op nageschakelde reinigingstechnologieën achter biomassa vergassers voor de productie van schoon gas, waaruit elektriciteit en warmte, transportbrandstoffen, chemicaliën en 'nieuwe gassen' (zoals SNG en waterstof) op een efficiënte wijze geproduceerd kunnen worden. Het biedt een overzicht van de huidige status van de belangrijkste partijen, de motieven en uitdagingen, en lopende R&D. Hoewel de opwaardering van biogas en stortgas niet beschouwd wordt als een R&D onderwerp binnen het EOS onderzoeksprogramma "vergassing, gasreiniging, conditionering en syngas productie", is in dit statusdocument ook aandacht besteed aan deze bestaande reinigings en conditionering technologieën. De technologieën in deze sector zouden ook toegepast kunnen worden op gas verkregen uit thermo-chemische conversie processen.

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Acknowledgement

Abbreviations and definitions

Ar	As received	MDEA	Methyl di ethanol amine
Bara	Bar absolute	MEA	Mono ethanol amine
BFB	Bubbling fluidized bed	MSW	Municipal solid waste
BTG	Biomass technology group	OLGA	Oil gas washer
CAPEX	Capital expenditures	OPEX	Operational expenditure
CCS	Carbon capture and storage	PAH	Poly aromatic hydrocarbons
CFB	Circulating fluidized bed	PP	Poly propylene
CGE	Cold gas efficiency	ppmv	Parts per million on a volume basis
Daf	Dry and ash free	PSA	Pressurized swing adsorption
Db	Dry basis	R&D	Research and development
DEA	Di ethanol amine	RD&D	Research, development and demonstration
ECN	Energy research Centre of the Netherlands	RDF	Refused derived fuel
EOS	Energy Research Subsidy	RFTC	Reverse-flow catalytic tar converter
ER	Equivalence ratio (lambda)	RME	Rapeseed oil methyl esther
ERS	Energy research subsidy	RPS	Rotating particle separator
ESP	Electrostatic precipitator	SNG	Substitute natural gas
FCC	Fluid cat cracker	TARWATC	Tar water cleaning
FICFB	Fast internally circulating fluidized bed	TOC	Total organic carbon
FP$_{number}$	European framework program	TREC	Tar reduction with char
GHG	Green house gas	TSA	Thermal swing adsorption
HC	Hydrocarbons	TUD	Technical university of Delft
HDS	Hydrodesulfurisation	TUe	Technical university of Eindhoven
HGF	Hot gas filter	TUV	Technical university of Vienna
HHV	Higher heating value (= Gross heating value)	UT	University of Twente
IGCC	Integrated gasification combined cycle	VPSA	Vacuum pressure swing adsorption
LT	Long term	wt%	Weight percent

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Summary

In order to stimulate the dissimination of knowledge, status reports are published by relevant stakeholders upon request from the Dutch Agency for Innovation and Sustainability (SenterNovem). The status report on gas cleaning focuses on cleaning technologies downstream biomass gasifiers to manufacture clean gas, from which electricity and heat, transport fuels, chemicals and 'new gases' (such as SNG and hydrogen) can be produced efficiently. This report provides an overview of the current status, the key players, the motives and challenges, and the ongoing remaining R&D. Although upgrading of biogas or landfill gas is not considered to be a R&D topic within the EOS research area "gasification, gas cleaning, conditioning and syngas production", the status report at hand also provides information focused at these existing upgrading technologies. The technologies in this sector may also apply for gas obtained from thermo-chemical conversion processes.

Gasification of biomass results in a producer gas containing numerous contaminants like dust, tar, (organic) sulphur, nitrogen and chlorine compounds, as well as alkali and heavy metals. Although concentrations could be relatively low depending on the feedstock used and the type of gasifier applied, at least some of these contaminants have to be destructed or removed upstream the final application of the producer gas, whether it is a boiler, gas engine or turbine, fuel cell or synthetic application. Hence, gas cleaning is inevitable in general, whether it is on tar components or non-tar components.

Still not many gasifiers are operating commercially on biomass feedstock, in particular when not taking into account those gasification systems (co-)firing the product straight into boilers. The need for gas cleaning, and in particular tar removal technology, for CHP or synthesis purposes is still the Achilles heel of biomass gasification and gas cleaning. Standard technology has proven to be insufficient for tar destruction or removal and has lead to years of (still ongoing) RD&D on thermal and catalytic tar cracking as well as (advanced) scrubbing technologies. For the moment, the latter ones seem to have made the biggest progress, with operating biomass based CHP plants at *e.g.* among others Harbøøre and Güssing, and water as well as organic liquid (RME, oil) based technologies being commercially available.

A step by step approach could be considered in which technology is scaled up gradually. There has been a tendency to construct large (demonstration) facilities hoping that these are operated successfully and due to scale are commercially attractive as well. The risks are high though, as solving unexpected issues will require enormous budgets. The risk that such a plant becomes mothballed instead of a commercial success has been proven to be relevant. Examples of this are the 180 ton per day Battelle gasification plant in Burlington, USA, and the 8 MW$_e$ ARBRE combined-cycle plant in Eggborough, UK.

Similar to tar removal technology, standard commercially available technology for removal of non-tar components up to now has also proven to be insufficient, in particular for critical applications of the producer gas in fuel cells or synthesis applications. Part of that has to do with upstream tar removal to be either insufficient (*i.e.* to low efficiencies of the tar removal) or not designed for the more stringent producer gas specifications for these applications (*i.e.* trace tar components still present in the gas). Another part of that is caused by the presence of gas contaminants previously not considered problematic for CHP applications (*e.g.* organic sulfur, dioxins). As can be expected, the biggest progress towards gas cleaning for non-tar components is made by those who are skilful at tar removal.

Over the years there has been a tendency for biomass gasification and gas cleaning to apply conventional technology or mimic coal gasification systems. For the gasification process this philosophy already has been dropped. Also the need for pressurised biomass gasification seems to be abandoned, argued by the complexity of biomass feeding. All commercially running biomass based gasifiers operate at (near) atmospheric pressure, not at the pressure levels of 30 bars and higher, typical for coal and oil based gasifiers.

Concerning gas cleaning, whether it is removal of tars or non-tar components, the operating conditions for commercially available conventional technology (*e.g.* coal based) will differ significantly from the conditions downstream a biomass gasifier, hence the feasibility of conventional technology will have to be reconsidered or at least tested it in realistic conditions. It might well be that conventional technology is not suitable for biomass based processes.

One of the lessons learned most in RD&D of gas cleaning is that conventional technology is not always applicable without any problems in thermo chemical conversion of biomass. Not only will the producer gas always contain unfamiliar (trace) components, also in many cases operating conditions like temperature and in particular pressure will be different from the conventional operating conditions of the technology just because it is not (yet) possible to operate the thermo chemical conversion process at these conditions. For that reason, it makes sense to test conventional technology first on realistic "biomass based" gases and conditions before installing them on large scale. It could be that due to the different gases and conditions (for the moment) thermo chemical biomass conversion systems need different technologies than bio chemical conversion systems or even thermo chemical coal conversion systems and these have to be developed step by step. A step by step approach becomes even more important for systems with multiple process steps, e.g. biomass gasification based synthesis systems like the production of Substitute Natural Gas (SNG), DME and Fischer-Tropsch (FT) diesel. For the successful development of these complex systems, slipstream testing of the critical catalytic components in gas cleaning and synthesis in an upscaled (demonstration) CHP plant consisting of the upstream gasifier and tar removal could benefit the RD&D of the whole system, as it enables long duration tests with the critical components under realistic gas conditions.

Samenvatting

Ter stimulering van kennis dissiminatie worden door relevante belanghebbenden op verzoek van het Nederlandse agentschap voor duurzaamheid en innovate (SenterNovem) status rapporten gepubliceerd. Het status rapport over gasreiniging richt zich op nageschakelde reinigings technologieën achter biomassa vergassers voor de productie van schoon gas, waaruit elektriciteit en warmte, transportbrandstoffen, chemicaliën en 'nieuwe gassen' (zoals SNG en waterstof) op een efficiënte wijze geproduceerd kunnen worden. Het biedt een overzicht van de huidige status van de belangrijkste partijen, de motieven en uitdagingen, en lopende R&D. Hoewel de opwaardering van biogas en stortgas niet beschouwd wordt als een R&D onderwerp binnen het EOS onderzeksprogramma "vergassing, gasreiniging, conditionering en syngas productie", is in dit statusdocument ook aandacht besteed aan deze bestaande reinigings en conditionering technologieën. De technologieën in deze sector zouden ook toegepast kunnen worden op gas verkregen uit thermo-chemische conversie processen.

Vergassing van biomassa leidt tot de productie van gas met tal van verontreinigingen zoals stof, teer, (organisch) zwavel, stikstof en chloorverbindingen, evenals alkali en zware metalen. Hoewel de concentraties relatief gering kunnen zijn, afhankelijk van de gebruikte brandstof en de aard van de vergasser toegepast, dient minimaal een aantal van deze componenten omgezet of verwijderd te worden voordat het gas ingezet kan worden, hetzij in een ketel, gasmotor of turbine, brandstofcel of synthetische toepassing. Met andere woorden, normaliter is gasreiniging onvermijdelijk, of het nu verontreinigingen in de vorm van teer componenten of niet-teer componenten betreft.

Commercieel gezien worden er nog weinig vergassers op biomassa bedreven, zeker wanneer geen rekening wordt gehouden met de (co-)vergassing systemen waarbij het productgas rechtstreeks omgezet wordt in ketels ten behoeve van warmte productie. De gasreiniging, en met name het verwijderen van teren, voor WKK of synthese doeleinden is nog steeds de achilleshiel van biomassa vergassing. Conventionele technologie heeft bewezen onvoldoende teren om te zetten of te verwijderen en heeft geleid tot jaren van (nog steeds voortdurende) RD&D op het gebied van thermisch en/of katalytisch kraken van teer alsook op het gebied van (geavanveerde) wastechnologieën. Vooralsnog is in de wastechnologieën de grootste vooruitgang geboekt, met de werkende WKK-installaties van onder andere Harbøøre en Güssing als voorbeeld. Wastechnologieën gebaseerd op water alsmede organische vloeistoffen (RME, olie) zijn commercieel verkrijgbaar.

Voor de ontwikkeling en opschaling van technologieën kan een stapsgewijze benadering gehanteerd worden. Het is een tijd lang de tendens geweest om direct grote (demonstratie) plants te bouwen in de hoop dat deze direct succesvol bedreven konden worden en tevens commercieel gezien aantrekkelijk konden zijn. De risico's hierbij zijn echter groot, en het oplossen van problemen vereist veel tijd en geld. Het risico bestaat dat een dergelijke installatie als gevolg hiervan wordt stilgelegd, in plaats van dat het een commercieel succes wordt. Voorbeelden hiervan zijn de 180 ton per dag Battelle vergasser in Burlington in de Verenigde Staten van Amerika en de 8 MW$_e$ ARBRE STEG in Eggborough in het Verenigd Koninkrijk.

Vergelijkbaar met de teerverwijdering, is toepassing van conventionele gasreiniging voor de verwijdering van niet-teer verontreinigingen tot nu toe onvoldoende succesvol geblemen, met name daar waar het de reiniging betreft voor de meer kritische toepassingen van het product gas, i.e. in brandstofcellen of synthetische processen. Deels heeft dit te maken met een onvoldoende functionerende teer verwijdering, anderzijds met het altijd nog aanwezig zijn van sporen van teercomponenten. Daarnaast bevat het product gas vaak nog een aantal additionele verontreinigingen, voor WKK-toepassingen niet als een probleem worden beschouwd (bv. organische zwavelverbindingen, dioxines), maar voor katalytische processen schadelijk kunnen zijn. Zoals kan worden verwacht wordt de grootste vooruitgang in de reiniging van deze niet-teer componenten gemaakt door degenen die op in staat zijn eerst in voldoende mate teren uit het productgas te verwijderen.

In de loop der jaren is er altijd een trend geweest om voor vergassing van biomassa en reiniging van het productgas gebruik te maken van conventionele technologieën en kolen gebaseerde systemen. Voor de daadwerkelijke vergassing van biomassa lijkt deze filosofie al te zijn vervallen. Ook de behoefte aan drukvergassing van biomassa lijkt te zijn vervallen, dit ten gevolge van de complexiteit van de voeding van de biomassa. Alle commerciële biomassa vergassers werken op (bijna) atmosferische druk, en niet op een (voor kolen of olie vergassers typische) druk van 30 bar en hoger. Met betrekking tot de gasreiniging, of het nu de teer of de niet-teer componenten betreft, lijken de bedrijfscondities voor biomassa systemen dusdanig te verschillen met die voor kolen systemen, dat de toepassing van conventionele technologieën heroverwogen zou moeten worden of dat minimaal de conventionele technologie onder voor biomassa systemen realistische omstandigheden getest zou moeten worden. Het kan goed zijn dat de conventionele technologie uiteindelijk niet geschikt blijkt te zijn voor biomassa gebaseerde processen.

Een van de grootste lessen in RD&D op het gebied van gasreiniging is wel dat conventionele technologie niet altijd zonder problemen toegepast kan worden in biomassa gebaseerde thermochemische conversie systemen. Niet alleen zal het productgas altijd sporen bevatten aan specifieke verontreiningingen, in veel gevallen zullen de bedrijfscondities zoals temperatuur en druk afwijken van de bedrijfscondities waarvoor de conventionele technologie was ontwikkeld en ontworpen, simpelweg omdat de thermochemische conversie van biomassa onder andere condities plaats vindt dan de biochemische conversie of de thermochemische conversie van kolen. Om die reden is het zinvol om conventionele technologie eerst te testen op realistisch productgas voordat deze grootschalig geïmplementeerd wordt. Het zou kunnen zijn dat als gevolg van de afwijkende samenstelling en condities van het productgas biomassa gebaseerde thermochemische conversie systemen (in eerste instantie) een gasreiniging vergt die afwijkt van de conventionele gasreiniging voor bio-chemische conversie systemen of zelfs thermo chemische omzetting van kolen. Stapsgewijze ontwikkeling en opschaling van dergelijke nieuwe technologieën kan hierbij van groot belang zijn, zeker voor systemen met meerdere nageschakelde processtappen, zoals synthetische processen voor de productie van Substitute Natural Gas (SNG), DME en/of Fischer-Tropsch (FT) diesel. Om tot een succesvolle ontwikkeling te komen van dergelijke complexe systemen kan het verstandig zijn om de kritische componenten in (katalytische) gasreiniging en synthese te testen in een slipstream van een bestaande opgeschaalde (demonstratie) WKK-installatie, bestaande uit de juiste vergasser en basis gasreiniging. De RD&D op het gebied van de noodzakelijke nageschakelde processstappen kan op die manier veel efficiënter plaatsvinden, aangezien de mogelijkheid bestaat om de kritische processtappen gedurende langere tijd onder realistische omstandigheden te kunnen testen.

1.   Introduction

1.1   The Energy Research Subsidy (EOS) programme

The government wants to help realize an affordable, reliable and clean energy economy, while fully acknowledging the role the market ought to play in this development. The role of the Energy Research Subsidy (EOS) programme is to initiate and support the necessary innovation processes. In some cases the market itself is already moving fast. The only help that may be needed then is with demonstrating a new technology. In other cases an idea may be in an early stage. Then the road to market introduction may be a long one and often help will be wanted. Biomass energy research is extremely important in achieving the aforementioned objectives. This research has been divided into three main areas, being *(i)* biorefining, *(ii)* electricity and heating, and *(iii)* gasification, gas cleaning, conditioning and syngas production. While the EOS programme can thus offer support at each of the stages of the energy innovation trajectory, it also helps the supply of knowledge to better meet the demand of the market.

1.2   The status report gas cleaning

In order to stimulate the supply of knowledge status reports are published by relevant stakeholders upon request from the Dutch Agency for Innovation and Sustainability (SenterNovem). The status report on gas cleaning focuses on cleaning technologies downstream biomass gasifiers to manufacture gaseous semi-manufactured products, whereby electricity and heat, transport fuels, chemicals and 'new gases' (such as SNG and hydrogen) can be produced efficiently. It provides an overview of:

- ➢ Current status
- ➢ Key players
- ➢ Motives and Challenges
- ➢ Required R & D work

Although upgrading of biogas or landfill gas is not considered to be a R&D topic within the EOS research area "gasification, gas cleaning, conditioning and syngas production", the status report at hand also provides information focused at these existing upgrading technologies. The technologies in this sector may also apply for gas obtained from thermo-chemical conversion processes.

1.3   The distinction between tar and non-tar components

In the status report gas cleaning 2009, the above points are reported. The report is divided into two main sections, one discussing the issues concerning tar contaminants still being considered the Achilles heel of biomass gasification, and the other the issues concerning the remaining non-tar contaminants. For both the tar and the non-tar components, the report includes an overview of the current state of research, development and demonstration in the field of gas cleaning, both in the Netherlands, Europe and globally.

A description of *(i)* commercial facilities, *(ii)* pilot and demonstration initiatives, and *(iii)* research and development is the main part of the report. A distinction is made between technologies focussing on tar components (chapter 2) and non-tar components (chapter 3), with a description of tars and the main associated issues included in the appendices. The similarities with conventional technologies for upgrading biogas or landfill gas are described in chapter 4. The conclusions and recommendations are given in chapter 5 of this status report.

An overview of who is who in the field of gas cleaning is provided appendix C of this status report. If an update of this overview is considered to be necessary in time, the author will adjust the digital version of this report and will make it available via the publications website of the Energy research Centre of the Netherlands (www.ecn.nl/publications).

2. Tar components

Tars are still considered to be the major bottleneck or even stumbling blocks in the application of biomass gasification [2][10]. This holds for fluidised as well as updraft fixed bed based gasification performed at temperatures well below 1000°C, as tar contents in the raw gas can be up to several tens of g/m_n^3. A description of tars and the main associated issues are included in the appendices.

The cleaning from these organic species down to values that are acceptable for different downstream processes is of crucial importance for successful implementation of biomass gasification technology. Tar reduction measures can be classified in three main categories, being *(i)* tar cracking and reforming, *(ii)* mechanical tar removal and *(iii)* physical tar removal. In the following paragraphs, these measures are discussed and compared.

2.1 Tar cracking and reforming

2.1.1 Thermal cracking

On thermal tar cracking many studies have been conducted and reported in public literature [68][104]. These studies are of limited value for gas from biomass gasification plants as they are often conducted with model tar components from pyrolysis of biomass or coal. Thermal tar cracking however, is a proven method to remove tars in large-scale thermal waste treatment plants, for example in the process of ThermoSelect [i], where the gas is treated at temperatures of 1400-1600 °C for a residence time of seconds. In these conditions, the synthesis gas from the cracker will only contain low amounts of methane; all other thermodynamically unstable hydrocarbons are cracked.

The application of thermal tar cracking by burning part of the fuel has the disadvantage that the higher (gross) heating value (HHV) of producer gas is decreased significantly, making it more complicated to use this gas in conventional gas turbines or engines. Furthermore, the cold gas efficiency (CGE) of the process drops significantly by cracking all hydrocarbons, including interesting components like CH_4 (useful for producing substitute natural gas) and C_2H_4 (a bulk chemical). This is illustrated in table 2.1, in which an air blown circulating fluidised bed gasifier operated at 850°C is taken as a reference and where the producer gas is partially combusted with air in a thermal cracker [68].

Table 2.1 *Effect of thermal tar cracking on the producer gas and the process efficiency*

$T_{gasifier}$ (°C)	$T_{cracker}$ (°C)	Required ER (-)	HHV producer gas (MJ/m_n^3)	CGE (%)
850	-	0.21	7.3	82
850	1100	0.28	6.0	76
850	1200	0.31	5.3	72
850	1300	0.34	4.8	69

Roughly, it can be said that every 100°C temperature rise results in a decrease of the calorific value of the producer gas by 0.5 MJ/m_n^3 or a decrease in cold gas efficiency of about 3.5%. Research performed at ECN showed that for thermal cracking of biomass tars to a level of below 100 mg/m_n^3 the temperature should be raised to a minimum of 1150°C [68], resulting in a CGE loss of approximately 8%.

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i   The process is owned by the ThermoSelect company (www.thermoselect.com) with licensees provided to JFE and Daewoo

At the Technical University of Eindhoven (TUe) in recent years research also has been carried out towards non-catalytic partial oxidation with the aim to reduce biomass gasification gas tar contents [51][52]. Experiments were performed within the temperature range of 900-1150°C and a residence time varying between 1 and 12 seconds. Brandt [22] reports temperatures and residence times needed of 1250°C and 0.5 seconds, respectively. In line with this result is the study of non-catalytic partial oxidation at FZ Karlsruhe [54][55]. This would lead to the disadvantages of the use of expensive alloys for the tar cracker and, moreover, significant exergy losses in the system. Also, soot is reported to be produced in this tar cleaning method. Recently, the Nexterra company [ii] announced that they had been running such a system in a slipstream of their pilot-plant updraft gasifier in Kamloops and are aiming on installing a gas engine downstream.

The research at the TUe now focuses on the working mechanisms behind partial oxidation in order to acquire the additional knowledge needed to optimize this technology [103]. In tar conversion by partial oxidation, observations are made indicating the significant role of oxygen radicals. The objective of this research is to map the influence of radicals on tar conversion at high temperature immediately after the gasifier unit and to develop a novel technology that combines the benefits of existing technologies. The basic idea behind the tar conversion by flame generated radicals is presented in figure 2-1.
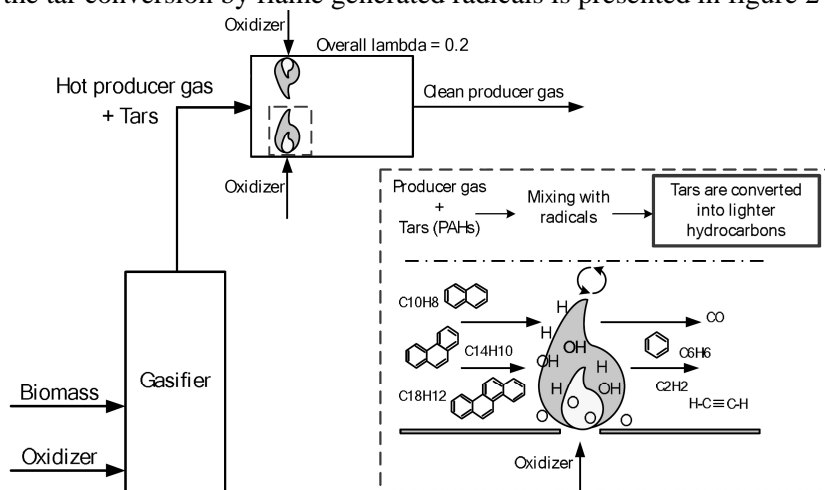
Figure 2-1 *Tar conversion by flame generated radicals*

2.1.2 Plasma enhanced cracking

Conventional gliding discharges are produced between two horn shaped electrodes placed in a relatively fast gas flow in the direction of the flow. They start at the spot where the distance between the electrodes is shortest, and spread by gliding progressively along the electrodes in the direction of flow until they disappear by themselves after a certain path. Figure 2-2 gives a schematically presentation of the GlidArc process [30], with the gas flowing from the bottom (injection point) to the top. In the gliding discharge, highly energetic electrons are produced, which results in species like ions, secondary electrons, UV radiation, radicals, excited molecules and molecules with attached electrons. This reactive medium, the plasma, is in this project used for the conversion of tar.
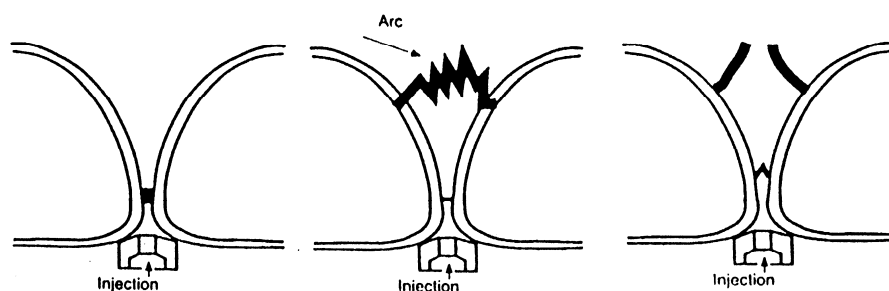
Figure 2-2 *Start, life and disappearance of the GlidArc discharges*

[ii] Communication with Nesho Plavsic during the 2008 Montreal IEA meeting for Bioenergy Task 33 on biomass gasification

The GlidArc plasma is combined thermal and cold plasma. About 20% of the energy is dissipated in the thermal part and 80% in the cold part [32]. The thermal part of the plasma is responsible for the plasma activity; in the cold part radicals are responsible for the removal of tars, similar as in the partial oxidation process. The production of radicals in a plasma process is facilitated by electrons in the plasma. The energy level of the electrons must be high enough in order that molecular bonds can be broken and radicals be produced in the plasma. For the GlidArc process the energy level of the electrons in the cold plasma revealed to be too low, as a result of which production of radicals is restricted and in addition the functionality for the removal of tars is too low. The tar conversion in the GlidArc reactor was during tests at ECN at most 40% [100]. Another reason for the low conversion is that the GlidArc plasma does not show any selectivity towards hydrocarbons, not even with increasing temperature. As a result, tar-like compounds as well as other hydrocarbons like methane, ethane, ethylene and benzene are equally converted [100], hence requiring significant amounts of energy for conversion of tars.

In contrast to the poor tar removal results in biomass fuel gas, high conversions can be obtained for the removal of hydrocarbons like toluene and xylene in air [32]. This can be explained by the fact that plasma in air facilitates low-temperature oxidation. Oxygen and in particular nitrogen radicals play an important role in this process, so the air is essential for the efficiency of the plasma assisted hydrocarbon decomposition. Recent research at the TUe revealed that in absence of nitrogen radicals, conversion is far less, possibly due to the fact that the oxygen radicals (unlike nitrogen radicals) can cause reformation of tars as well. In the commercial plasma processes constructed by *e.g.* the Plasco Energy Group [iii] the generated arc is pushed into a furnace by means of air, hence creating the right conditions. No results on the Plasco plant are published though up till now. In producer gas, the hydrocarbons cannot be "ignited" as the reaction rate with CO_2 or H_2O is much lower than the reaction rate with air. Therefore, the conversions are much lower [100]. An alternative to the GlidArc plasma is a thermal plasma reactor, removing tars at high temperature. An advantage of this plasma reactor in comparison with a thermal tar cracker is the fast and good controllability of the temperature in the reactor without diluting the gas with inert compounds like N_2 and CO_2. Due to the high consumption of electric energy, a sole thermal plasma reactor, however, can not compete energetically with a thermal tar cracker.

At the TUe research is done on fully non-thermal corono plasma for tar removal. The major advantage of using non-thermal plasma is to do chemical conversion of tars at low temperatures and solely rely on the generation of high energy electrons which dissociate molecules and thereby creates the necessary reactive environment. Experimental results have indicated complete conversion of tar by pulsed plasma processing at lower temperature [69]. The investigations also indicate that the gaseous environment, e.g. the presence of nitrogen, has strong influence on tar cracking reactions. As such, it can be expected that tar conversion in producer gas becomes less, in particular for gasifiers producing a gas with initial higher heating value (figure 2-3).
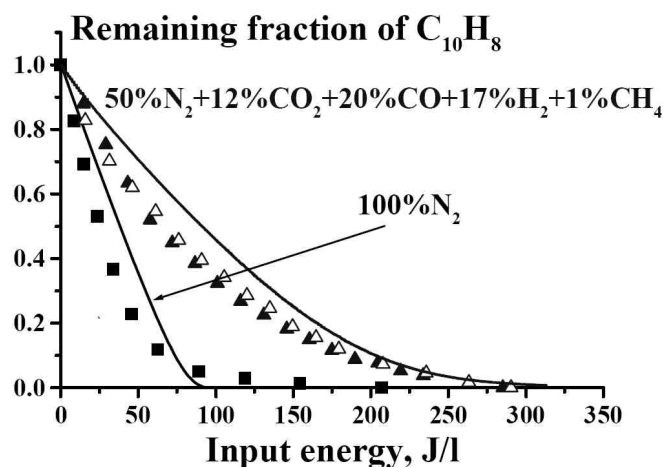
Figure 2-3 *Naphthalene conversion as a function of energy input for the corona*

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iii The Plasco Energy Group completed a plasma-arc waste demonstration plant in Ottawa, Canada at the Trail Road Landfill, to process 85 tonnes per day of municipal solid waste MSW (www.plascoenergygroup.com)

The explanation for the conversion of tars being less efficient in realistic producer gases might be found in the tar decomposition scheme *e.g.* that of naphthalene as presented in figure 2-4 [69]. The H and OH radicals can cause the desired decomposition of the naphthalene; however can also result in the reformation of naphthalene from the intermediate tar radicals. Hence, the more H and OH radicals one might expect present in the producer gas, the less the tar conversion efficiency will be.
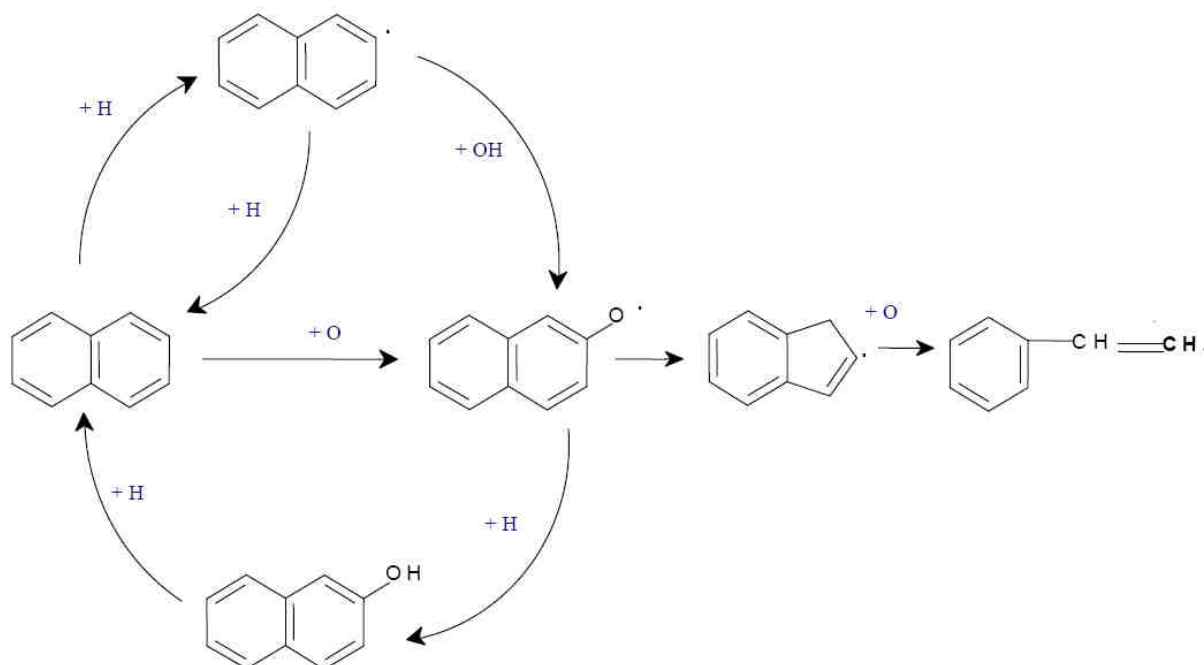
Figure 2-4 *Naphthalene radical decomposition scheme*

2.1.3 Catalytic cracking

Catalytic tar cleaning is potentially attractive as no additional energy input may be required and hence thermodynamic efficiency losses can be kept to a minimum [2]. Abu El-Rub [1] reviewed different tar cracking catalysts (figure 2-5), with the advantages and disadvantages summarized in table 2.2 .
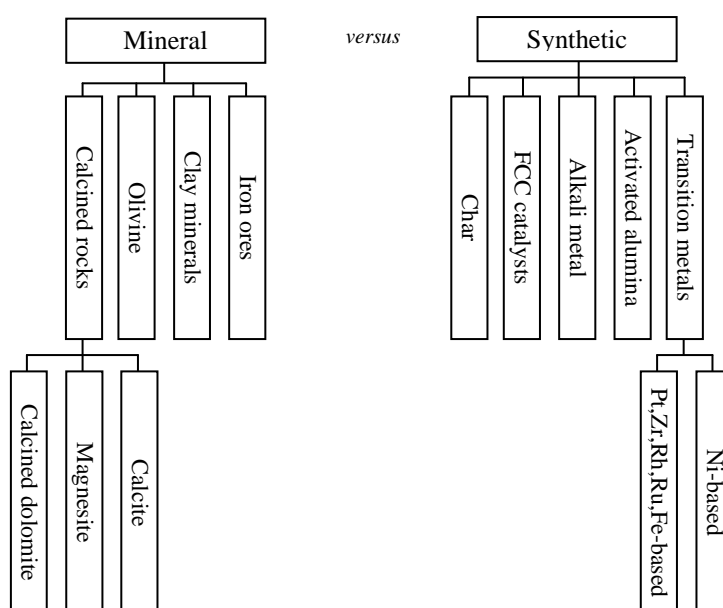
Figure 2-5 *Classification and types of catalysts used for tar reduction*

In this paragraph three different systems for catalytic tar cracking are discussed, based on addition of catalytic materials to the bed material of the gasifier (§2.1.3.1) or application of catalytic beds, monoliths or filters downstream the gasifier (§2.1.3.2 and 2.1.3.3).

Table 2.2   *Summary of tar cracking catalysts advantages and disadvantages*

| Catalyst	Advantages	Disadvantages
Calcined rocks	Inexpensive and abundant Attain high tar conversion ~95% conversion with dolomite Often used as guard beds for expensive catalysts Most popular for tar reduction	Fragile materials and quickly eroded from fluidized beds
Olivine	Inexpensive High attrition resistance	Lower catalytic activity than dolomite
Clay minerals	Inexpensive and abundant Less disposal problems	Lower catalytic activity than dolomite Most natural clays do not support the high temperatures (>800ºC) needed for tar reduction (lose pore structure)
Iron ores	Inexpensive Abundant	Rapidly deactivated in absence of hydrogen Lower catalytic activity than dolomite
Char	Inexpensive Natural production inside the gasifier High tar conversion comparable to dolomite	Consumption because of gasification reactions Biomass char properties not fixed and depends on biomass type and process conditions
FCC	Relatively cheap but not cheaper than the above More knowledge is known about it from the experience with FCC unit	Quick deactivation by coke Lower catalytic activity than dolomite
Alkali metals	Natural production in the gasifier Reduce ash handling problem when used as a catalyst	Particle agglomeration at high temperatures Lower catalytic activity than dolomite
Activated alumina	High tar conversion comparable to dolomite	Quick deactivation by coke
Transition metals	Able to attain complete tar reduction at ~ 900²C Increase the yield of CO and H_2 Ni-based 8 to 10 times more active than dolomite	Rapid deactivation because of sulfur and high tar content in the feed Relatively expensive

2.1.3.1 In bed materials

Natural minerals

Rock materials like *dolomite* and *limestone* are well known as catalytically active bed materials [2], in particular in their porous calcined form. Especially, the dolomites are among the most active and most widely used. They are comparatively active in tar conversion (up to 95%), cheap and are considered to be disposable, which is surely advantageous and this explains their popularity. The catalytic tar reduction potential however strongly depends on morphology factors (pore size, surface area) and content of other metals. Disadvantages are that the material is heterogeneous in nature (differing per region) and in particular that it is soft and thus relatively high attrition rates can be observed [35][43][87], leading to losses and increased solids loads to the gas cleaning. Furthermore, calcination is necessary for sufficient reactivity which involves significant energy input. Deactivation of calcined rock material is attributed to *(i)* carbon deposition and *(ii)* re-carbonation when CO_2 partial pressures are too high in the system [81][82]. In the 500 kW_{th} air-blown CFB gasifier at Umsicht, Germany, operating at 910-920°C the use of fresh dolomite led to tar concentrations in the gas of about 300 mg/m_n^3, however used dolomite resulted in values up to 2.5 g/m_n^{3} [53]. This in-time degradation effect is comparable with the data published by Cutec for their steam/O_2 blown 400 kW_{th} CFB gasifier [77]. Here, also, it was indicated that compared to the use of sand, dolomite showed the best reduction of tar. However, still values of 3.5 g/m_n3 were reported in the raw gas, which is significantly higher than reported by Ising [53] concerning the Umsicht CFB gasifier. Possibly this is an example of the heterogeneous nature of the dolomite used; also the different oxidizer could play an important role as an explanation for the difference observed. Companies having used, or still using the technology of in-bed use of calcined rock material are TPS, Carbona Inc., Foster Wheeler and Repotec (the latter at the Güssing plant in specific test campaigns).

Another naturally mineral with catalytic activity is *olivine sand*, which can be represented by the chemical formula $(Mg,Fe)_2SiO_4$. This mineral has also demonstrated tar conversion activity at in-bed use, both in atmospheric and pressurised fixed bed applications for biomass and biomass-plastic mixtures [9][25][77][79]. It appeared that giving a heat treatment to this mineral material under oxidising conditions had a significant positive impact on its activity [36][38]. Iron oxide, reduced and migrated to the outside of mineral particles is believed to play an important role, although also Ca is considered to be important in this respect [76]. The demonstration plant of Güssing uses olivine as a bed material, clearly showing catalytic activity, although differences are observed in different batches and origins of the material [76]. Research at ECN [105] revealed that the mineral becomes more active after some time of operation under reducing conditions, as was also observed by Rauch et al [76]. It was also observed that Austrian olivine is catalytically more active as a bed material than for example Norwegian olivine. This is shown in Figure 2-6, in which the carbon-in-tar to carbon-in-wood ratio is presented at different gasification temperatures. The difference between Norwegian olivine and sand as bed material on tar formation is limited, whereas Austrian olivine (as used commercially at the 7000 hours per year running Güssing plant [95]) is active, not only for converting tars, but also for converting methane, acetylene, and ethylene [105].
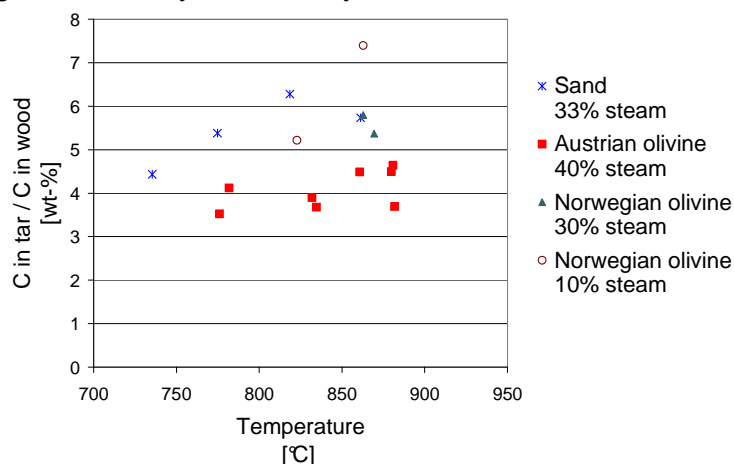
Figure 2-6 *Effect of in-bed olivine on tar formation*

The claimed advantage of olivine sand is its low price, which is in the same order as of dolomite: some 120 €/ton, in combination with a higher resistance against attrition [2]. Its claimed resistance against attrition as compared to dolomite though is arguable, as the research at ECN showed that the activity of the olivine is strongly dependent on the porosity of the olivine and the migration of iron oxide to the outside of the mineral particles [105]. High cracking activity might well be associated with low resistance against attrition, leading to losses and increased solids loads to the gas cleaning.

Alternative minerals reported and tested to be catalytically active include *bauxite*, natural *alumina*, clay minerals and *iron ore*. One of the latter ones was tested at ECN [105] as well and showed comparable results to Austrian olivine, although its catalytic activity could be related to the associated oxygen transport from the combustor to the gasification zone of the indirect gasifier via the circulating bed material. As in general these alternative minerals show lower activity than dolomite and olivine or are prone to deactivation as a result of coke formation [2], they are not commonly applied as bed materials.

Metallic and metal oxide synthetic catalysts
Conventional *nickel* steam reforming catalysts, designed for use in fixed bed applications, have been applied as in-bed tar converting catalysts. However they revealed not to be robust enough, as both coke formation and catalyst attrition led to rapid loss of activity [11][33]. Coke formation is associated with acidity of the catalyst surface and can be made less severe with the help of (earth)alkali oxides [80]. The catalysts have been adjusted to cope with the abovementioned disadvantages, *e.g.* by using nickel aluminates with lanthanum and cobalt as promoters [42]. Test results of nickel-based in-bed measures for tar reduction are not (yet) available, however up to 80% conversion of toluene as model tar component was achieved under lab conditions. The Co/Ni molar ratio seriously influenced the conversion activity, showing the following order: Ni-Al-La > Ni-Co-Al > Ni-Al [8].

Nickel has also been used to enrich the natural mineral olivine, creating a hybrid between natural material and artificial catalyst, making it more stable than the conventional artificial catalysts. Using up to 40 wt% of this material in an olivine bed led to about 75% decrease of tar content in the gas. The catalyst showed no noticeable deactivation in two tests with a fluidized bed biomass steam gasifier of 30 and 45 h, respectively [27][28][70][75].

At the University of Tsukuba, Japan, a *ruthenium* based catalyst ($Rh/CeO_2/SiO_2$) has been tested as an in-bed catalyst [3][4][5][6][7]. The addition of the SiO_2 prevented sintering of the catalyst, which was the biggest issue in tests with the Rh/CeO_2 based predecessor. Although no long-term tests were performed (yet), the indications are positive for this catalyst as practically no coke formation is observed and tar concentration in the final producer gas is reported to be negligible.

2.1.3.2 Catalytic beds and monoliths

As with in-bed materials, natural minerals and metallic and metal oxide synthetic catalysts can be used for tar conversion in downstream reactors. In this paragraph the progress made in tar conversion in downstream catalytic beds and monoliths is summarised.

Natural minerals

As described in §2.1.3.1 naturally occurring minerals are relatively cheap materials, and are disposable. Their softness and attrition rate are downsides. Also, chlorine present in the biomass fuel may react with CaO to produce $CaCl_2$ and thus reduce the catalytic activity [2]. A substantial amount of research on downstream beds with dolomite and limestone has been carried out worldwide by numerous companies and research institutes. The Swedish Company TPS applies this technology for tar reduction using calcined dolomite (together with oxygen) in a circulating fluidized bed situated downstream of the main air-blown biomass CFB gasifier [78]. Other natural minerals applied for downstream cleaning of tar components are bauxite (Al_2O_3/Fe_2O_3), bentonite ($CaO/Al_2O_3/SiO_2$) and other natural mixed oxides [53]. With inlet concentrations of real tar of the 500 kW_{th} Umsicht CFB gasifier, more than 95% conversion of tars was obtained with the dolomites and the bauxite, and about 75% with the bentonite.

Char

By using char as a catalyst for tar cracking a cheap material is used that is already available in large quantities from the biomass fuel itself. At Twente University as well as Karlsruhe University tests were performed showing that naphthalene conversions at 900°C were practically 100%. At 750°C with typical air-blown gasification gas compositions conversion above 95% was obtained with only little char being consumed [1][60]. Tests at ECN with the TREC [iv] reactor showed though that although char was able to reduce tars (with approximately 75%) it was not very selective for heavy tars. Performance could only be improved by applying more catalytically active bed materials like natural minerals [97].

Metallic and metal oxide synthetic catalysts

Among the artificial catalysts of the transition metal type, applied in downstream beds, nickel based ones are the most popular. Most commercial steam reforming catalysts being supplied by for example BASF, ICI, UCI, Haldor Topsøe and Südchemie all contain this element to a large extent [2]. Corella et al. [26] tested several commercial catalysts for the purpose of biomass gasification gas upgrading. They indicated changes in the main gas constituents occurring with the formation and destruction of methane. When applied at temperatures significantly lower than 900°C, sulfur species in the gasification gas had a poisonous impact on the catalyst activity and a negative effect on the required operating temperature of the catalyst. Also, the commercial reforming catalyst materials are sensitive to other gasification gas trace compounds, like alkali and chlorine species. Moreover, loss of material has been reported [12]. Furthermore, rapid deactivation due to coking has been mentioned by many researchers.

[iv] TREC being the abbreviation of Tar REduction with Char

Worldwide a substantial amount of research work has been dedicated to investigation of conventional, commercial nickel based catalysts, and only a small part will be mentioned in the report at hand. In the Netherlands, at BTG commercial nickel based catalysts have been applied in a reverse-flow catalytic tar converter (RF®TC) [92]. Raw producer gas from a biomass gasifier is fed to the reactor at a temperature between 350 and 650°C, hence above the tar dewpoint and heated up at the entrance section to the desired reaction temperature of 900-950°C. The commercial Ni-catalyst is placed in the centre section of the reactor. Tar components, as well as light hydrocarbons including methane, are converted into CO and H_2. Additionally, nearly all NH_3 is removed. To counterbalance these endothermic reactions air is added to the reactor (about 5% of the producer gas flow). The catalyst used has been tested for over 6000 hrs with wood-derived producer gas. During this period no detectable change in catalyst activity was observed, only when extra sulfur was added. After stopping the additional sulfur supply the original catalyst activity was achieved again. In 2002, BTG implemented the developed RF®TC together with a rotating particle separator (RPS, §2.2.2) downstream a farm-scale poultry litter gasifier system [23]. The whole plant was stopped in 2004 due to problems with the RPS [93].

Research on monolith reactors with Ni-based coating has been performed at different locations in Europe. Monoliths are ceramic blocks of parallel, straight channels on the wall of which a thin layer of catalytically active material is deposited [29][61]. The honeycomb structure of these monoliths tolerates gas loaded with particulate matter. Figure 2-7 shows a typical monolith element [53][62]. Toledo et al. [91] concluded that with coated monolith elements tar levels below 200 mg/m_n^3 can be attained, but the lifetime of the monoliths is very much dependent on the configuration that is chosen to ensure a temperature profile that prevents the occurrence of too high or too low temperatures at the entrance and exit of the monoliths. Also, the feedstock should contain low alkali content, or at least the alkalis should be removed before reaching the monoliths face, as stickiness problems can occur due to the presence of these trace metal species.

Figure 2-7 *Tar reforming monolith and monolith reactor unit*

At Umsicht the Ni-based monolith process was tested for 500 hours downstream the 500 kW$_{th}$ CFB gasifier, resulting in lower than 50 mg/m_n^3 tar levels, which were aimed at [53]. It showed no significant deactivation, claimed to be also due to periodic cleaning of the monolith unit. The monolith catalyst was scheduled to be tested at the Güssing plant [71], results of these tests have not yet been published. At VTT also a nickel based tar reformer is being developed. In the European FP6 project BIGPower the monolith catalytic tar converter is positioned downstream the 30 MW$_{th}$ Carbona (nowadays Andritz) pressurised gasifier and upstream of a producer gas cooler and a lower temperature filter at the demonstration site in Skive, Denmark [62]. Slip stream testing at the Güssing plant in Austria revealed that almost complete tar and considerable ammonia decomposition could be achieved over this catalyst at temperatures above 850°C. The initial tar content of the gas was however already relatively low, in the order of 1.5 g/m_n^3. The published information on methane conversion [49] suggest though that deactivation of the catalyst due to sulfur poisoning was severe (within hours), and that temperatures had to be kept high (above 900°C). At Skive, where similar low initial tar concentrations might be expected due to the application of dolomite as bed material, commissioning of the plant with the VTT tar reformer has started, however the project is delayed and the official opening is postponed to 2009. The delay reflects the inherent uncertainty related to large-scale demonstration of the new technology [46].

As an alternative to the nickel based catalysts, also a lot of R&D has focussed on catalysts based on iron, palladium, ruthenium, cobalt, molybdenum, magnesium oxide, zirconia or combinations of those. Reported tar conversion efficiencies and catalysts lifetimes up till now [2][33] however do not suggest that these catalysts are nearer to commercial implementation than the nickel coated monolith reactors.

2.1.3.3 Catalytic filtration

An alternative to catalytic in-bed materials or downstream catalytic beds is catalytic filtration. This combination of ceramic gas filtration and catalytic tar cracking [45] is being developed by among others Pall (Schumacher) and Madison Filter (in cooperation with Haldor Topsøe) and is a method for particulate removal from hot gases, as by using this method the gas flow can maintain its sensible heat resulting in a higher thermal efficiency compared to the other methods [2]. A filter to remove particles from fluidised bed gasification processes is necessary, as cyclones (even multiple ones in series) are not good enough to eliminate the smallest particulates, whereas for downstream equipment this often is required (§3.6.1).

In a two step approach of separated catalytic cracking and filtering, the disadvantage of placing the catalyst unit upstream the filter is the fast deactivation of the catalyst by particle deposition. The disadvantage of placing the catalyst unit downstream the filter is the necessity of having two (expensive) high temperature process units as they should be operated above the tar dewpoint. The catalytic filter combines the two tasks of tar cracking and solids filtration into a single process step. The (ceramic) filter candles are impregnated with catalyst and can be compared to membrane reactors (as shown in figure 2-8) [2][45][47][66].
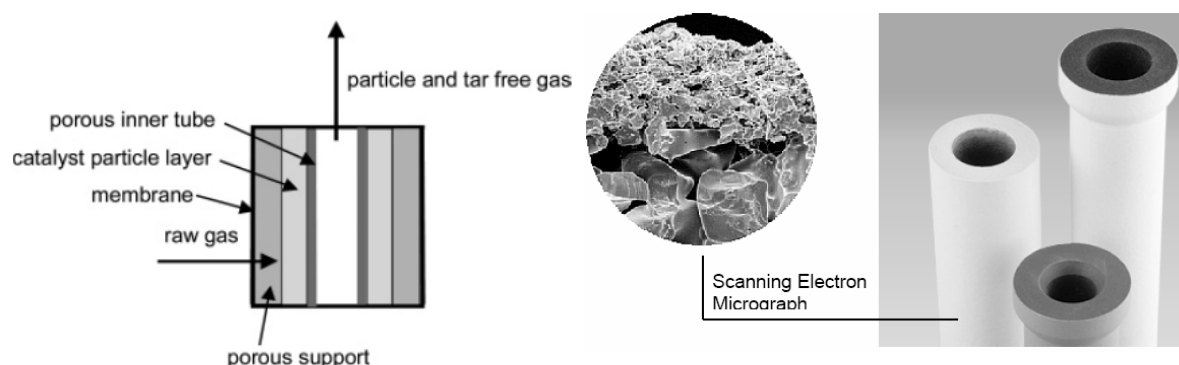
Figure 2-8 *Tar cracking catalytic filter and filter elements*

The impregnation with catalyst is either done by *(i)* applying a catalytic coating, *(ii)* adding the catalytic component to the ceramic grain and binder mixture or *(iii)* by using a porous inner tube fixed at the head of the candle to allow integration of a catalyst particle layer [66]. Considerable success under the conditions proposed, for ruthenium at above 900°C and for nickel between 750 and 900°C, has been achieved, but there is a fundamental limitation to the approach in that, at the temperatures required by the catalysts, alkali metal compounds are mostly still volatile. A second, lower-temperature solids removal step will therefore still be required after these components have condensed [47].

2.2   Physical tar removal

Physical tar removal is mainly done on the basis of electrostatic precipitators [102], rotating particle separators [98], cyclone separators, filters (either baffle, fabric or ceramic), or scrubbers (either water or organic liquid based) [37][47]. Many of these technologies are applied in combination with each other or with catalytic tar removal technologies as often they are not only removing tars, but also particulates like dust and non-tar components like NH_3 (as discussed in chapter 3). In the following paragraphs, however, mainly their application as physical separator of tars will be discussed.

2.2.1 Electrostatic precipitators

Electrostatic precipitators (ESPs) are widely used to remove fine solids and liquid droplets from gas streams. Although effective with liquid droplets, they prove inefficient when "tar" is in the gaseous phase. This means that, when the target is the "tar" removal, high-temperature operation should be avoided. In such a case gas should be quenched before ESP use (figure 2-9). The basic principle of a wet ESP is gas ionisation upon passing between a high voltage electrode and an earthed (grounded) electrode. The ions are produced in a corona discharge and attach themselves to dust particles or droplets of tar and water. Particles and droplets become charged and are attracted to the grounded electrode due to the electric field. The precipitated dust and droplets flow to the bottom of the ESP where they are collected [100]. Only wet ESP can be used to remove "tar" from biomass gasifier gas, because "tar" condensation on dry ESPs precipitation electrode would progressively inhibit particle removal [65].
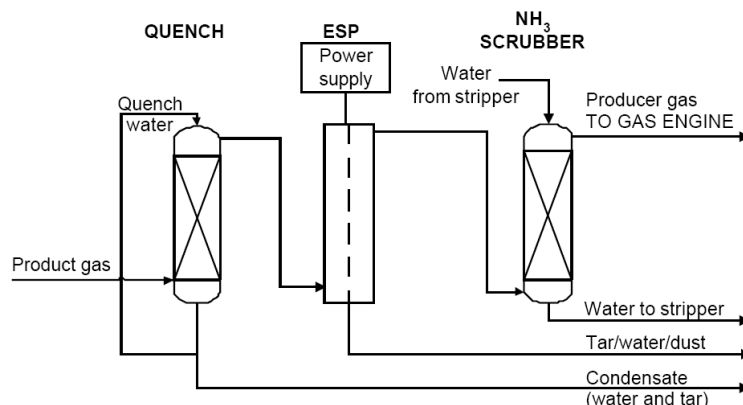
Figure 2-9 *ESP based tar cleaning*

Wet ESP has successfully been applied for electricity generation with gas engines downstream an updraft gasifier in Harboøre (§2.2.5), where the gas is quenched with water, and downstream a downdraft gasifier in Wiener Neustadt, where the gas is quenched with RME (§2.2.6). At ECN, a wet ESP was installed downstream a circulating fluidised bed gasifier with water quench and also here, the ESP efficiently removed dust and condensable tar droplets from the producer gas [100]. The wet ESP at ECN therefore was also integrated in the oil gas washer OLGA for removing dust and tar aerosols downstream the collector column (§2.2.7). The wet ESP is often integrated in the tar scrubbing technologies.

2.2.2 Rotating particle separators

The rotating particle separator (RPS) uses a rotating cylinder, which is centred in a single cyclone. The RPS was successfully implemented for de-dusting of flue gas in combustion systems without associated tar and lead to research on tar removal via RPS as well. For tar removal research two methods were considered, one based on condensation of tars and subsequently removing the droplets of condensed tars from the gas and the other based on injection of a solvent and subsequently capturing saturated solvent [67].

For cleaning of producer gas with the RPS operating in dry mode, useful practical experiences were obtained at the ETH in Switzerland. The RPS was initially tested as a dust filter operated at temperatures above the tar dewpoint downstream a downdraft gasifier. Although the filter operated successfully, it did not capture tars as the operating temperature of the RPS was above the typical tar dewpoint of a downdraft gasifier. During operation of the RPS in dry mode for the removal of organic contaminants [67], separation of heavy tars was observed to be better than for the other components, however very limited with reduction of 30 to 70% reached at temperatures between 130 and 140°C. Research on tar removal with a (wet) RPS at ECN [98] operated at a low temperature, at which water form the producer gas condensed, revealed that the filter element of the RPS blocked by in particular heavy tars within hours after start of the tests (figure 2-10). Cleaning of the filter element by continuous water spray was not sufficient. Although RPS could effectively remove dust, tar aerosols and NH_3, the fouling issue with heavy tars caused the research on RPS to be stopped.
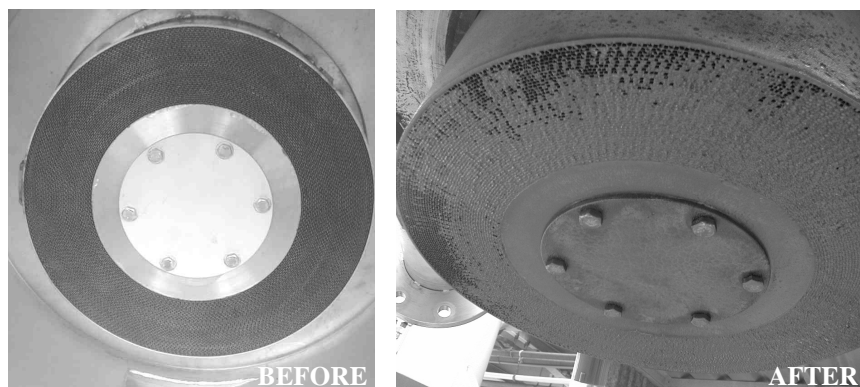
Figure 2-10   *Rotating particle separator before and after testing at ECN*

BTG went on developing and implemented an RPS together with their own developed RF®TC (§2.1.3.2) downstream a farm-scale poultry litter gasifier system [23]. The whole plant was stopped in 2004 due to problems with the RPS [93].

2.2.3 Cyclone separators

Cyclone filters or centrifugal force separators are also mechanical technologies that can potentially be used for tar removal. These technologies operate on the same principles as those for particulate removal, using centrifugal force to separate solids and aerosols from gases. The technologies are best suited for removing larger particles, typically those with diameters of 5 µm or greater. In practice, cyclones and related centrifugal separators are not used for tar removal in biomass gasification systems, although interest has been expressed in the use these types of systems [67][84]. The combination of particulates and sticky tar in the gas stream, however, creates a deposition of material on cyclone surfaces that is difficult to remove in normal operation. Even if particulates were removed prior to tar condensation, cyclones are ineffective at removing small-diameter tar aerosols that include material below 1 µm size. As a result, cyclones are not a practical means of removing tars from raw biomass gasification products [84].

2.2.4 Filters

Over the years filters of various types have been used in biomass gasification systems for tar removal. The tars are captured by impingement of condensed aerosols on the filter surface. In contrast to solid particulates like dust, tar is more difficult to remove from the filter surface as it exists in a high viscous sticky liquid form. These differences in characteristics make many filters less suitable for tar removal than for particulate removal. Up till now filters, including fabric bag filters and ceramic hot gas filters, are generally inappropriate for tar removal [84], unless coated with a tar cracking catalyst (§2.1.3.2 and 2.1.3.3).

Application of packed or granular bed filters has been more successful historically for tar removal and even common practice in small scale gasification systems constructed during the 2nd world war. The packed or granular bed filters consist out of grains, such as sand, (lignite) coal or activated carbon, or sawdust. In some experiences with granular bed filters for the removal of tars as well as particles from biomass fuel gases are presented (table 2.3) [67].

Table 2.3   *Experiences with granular bed filters for tar removal from biomass fuel gases*

Filter material	Particles removal	Tar removal	Tar definition
Sand	73.0 - 99.8 %	50 - 97 % 68 - 98 % 97 - 99 %	Heavy tars 16 EPA PAH Phenols
Sieved lignite coke	Not determined	50 - 97 % 100 %	Heavy tars 16 EPA PAH
Saw dust	94.0 - 99.5 %	83 - 85 % 50 - 67 %	Condensables at 5°C Condensables at 5°C plus PAH

While packed or granular bed filters provide adequate filtration of tars, they still create operational problems related to cleaning the filter as well as to waste disposal. These filters may be appropriate for small systems operating in remote locations where labour is inexpensive, but they are not being incorporated into designs for larger-scale commercial facilities due to operational and cost considerations, unless as final guard bed [84].

2.2.5 Water scrubber

A water based scrubber tar removal technology has been in operation since 2000 at the Harboøre updraft gasification plant in Denmark, operating on wood chips [89]. The technology has also been licensed to the Japanese company JFE and the German company Relax Umwelttechnik®. The producer gas from the reactor contains about 80 g/m_n^3 of various tars and acids. The gas temperature downstream the reactor is about 75°C. The producer gas is cooled serially through two district heating shell and tube heat exchangers in which a large amount of tar and water is separated together with most of the particles. Following this the gas is cleaned for remaining water/tar aerosols and dust in a wet ESP (§2.2.1). After these processes the contents of tar and dust are both below 25 mg/m_n^3, and the gas is suitable for fuelling gas engines.

Figure 2-11 *Process scheme of the Harboøre process with water based tar scrubber and wet ESP*

This water based scrubbing technology results in a huge amount of tar-contaminated water. At the Harboøre plant every 1 kg of wood chips gasified results in approximately 0.6 kg of waste water [89]. This water is separated in a coalescer into *(i)* heavy (high molecular) tars having a net calorific value of about 27 MJ/kg (approximately 8% on a weight basis) and *(ii)* water contaminated with light (low molecular) tars and acids. The heavy tar is stored in a 150 m³ heated tank and part of this tar is used for district heating peak load firing in the oil/tar hot water boiler. The bulk water fraction can not be discharged because of its phenol, total organic carbon (TOC) and acid content and therefore cleaned in the tar water cleaning system (TARWATC).

The TARWATC uses hot water from the engine exhaust boilers to evaporate the contaminated water and to separate the light tars (having a net calorific value about 14 MJ/kg). The slightly contaminated steam is heated in counter-flow with clean steam from the TARWATC reactor to a high temperature before entering the reactor. The temperature is further increased by burning part of the light tars inside the reactor. The clean steam is condensed in a district heating cooled condenser and fulfils the environmental regulations for discharge into municipal systems [89].

Although the water based scrubbing technology is capable of cleaning the gas sufficiently for some applications [89] and the Harboøre plant operated 8000 hours in 2006 [96], the scrubbing technology shifts the tar problem to (expensive) treatment of wastewater [19].

2.2.6 RME scrubber

As an alternative to water based scrubbers oil wash can be applied as well. This has been done successfully downstream both the indirect gasification process in Güssing [47][48] and the downdraft gasifier in Wiener Neustadt, with the latter one having a wet ESP installed as well to capture tar aerosols (§2.2.6). Without an ESP installed, filters would be required for removing these aerosols before the gas can be applied in the gas engines.
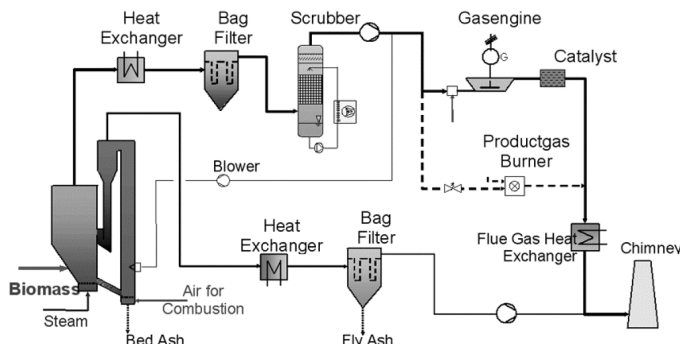

Figure 2-12   *Process scheme of the FICFB process with RME based tar scrubber*

The tar is almost completely removed by the scrubber using rapeseed oil methyl esther (RME) as a medium. After phase-separation of the condensate, the RME saturated with tar is recycled to the combustor of the indirect gasifier, which means that no liquid waste stream is produced. In order to be able to apply RME as scrubbing liquid, though, the initial tar concentration in the producer gas has to be relatively low, as otherwise the required amount of RME would be too large. At the Güssing plant, the tar concentration of the producer gas therefore is reduced to approximately 2.5 g/m_n^3 by using olivine as catalytic bed material [48]. Furthermore, the RME contributes significantly to the total ecological impact of the gasification process [41]. Application of the oil based OLGA tar removal technology (§2.2.7) instead of the RME scrubbing technology reduces this negative effect of scrubbing liquid consumption, as hardly any oil is consumed during operation.

2.2.7 OLGA

The oil gas washing technology OLGA developed by ECN and Dahlman [47][59] is based on a multiple stage scrubber in which the producer gas is cleaned by special scrubbing oil. In the first section of OLGA (the collector, figure 2-13) the gas is gently cooled down by the scrubbing oil. Heavy tars condense and are collected, after which they are separated from the scrubbing oil and can be recycled to the gasifier in order to serve as feedstock of the gasifier. As only tars are recycled to the gasifier, the amount of scrubbing liquid used is not limited like in the RME scrubbing technology (§2.2.6) and hence higher tar loads in the producer gas are acceptable. In the second stage of OLGA (the absorber / stripper), lighter gaseous tars are absorbed by the scrubbing oil. The tar-laden oil is regenerated in a stripper. In case of an air or steam blown gasifier hot air is used to strip the tars off the scrubbing oil. This air loaded with light tars can be used as the gasifying medium in the gasifier. Hence, the stripper column design is not only based on the tar removal capacity but also on the amount of air that can be used by the gasifier. All heavy and light tars can be recycled to the gasifier where they are destructed and contribute to the energy efficiency [73]. Tar waste streams are efficiently recycled this way [59].

The OLGA technology has been demonstrated downstream different gasifiers operated on a variety of fuels at ECN and in Moissannes, France [v]. Dahlman is realising an OLGA tar removal system for a gasification plant which will use 1 tonne per hour of chicken litter and/or forest residues as feedstock. At this moment, the plant is in the engineering phase. It is scheduled to be started in the autumn of 2009. Furthermore, Biomass Gas & Electric, SilvaGas, Dahlman and Solar announced that they are working towards the realization of an advanced biomass gasification plant, scheduled for completion in 2010 [v].

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v The gasifiers at ECN include CFB, BFB and indirect gasification processes, whereas the plant in Moissannes is based on a special updraft gasifier [59]. Feedstocks used for testing include wood, grape pulp and more recently fluff. More information can be obtained from the Dahlman OLGA technology website www.olgatechnology.com.
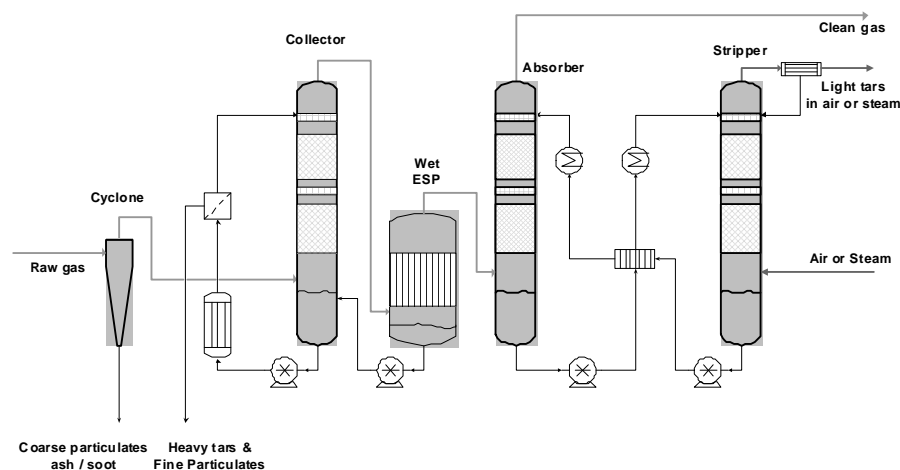
Figure 2-13   *Process scheme of the OLGA tar removal technology*

ECN operated and tested two aqueous systems and one oil based system, OLGA, downstream their 500 kW_{th} air blown circulating fluidized bed gasifier, producing a producer gas with an initial tar load of 10 to 20 g/m_n^3 on dry basis [v]. In figure 2-14 the tar removal efficiency of the three tested gas cleaning systems is compared [59].

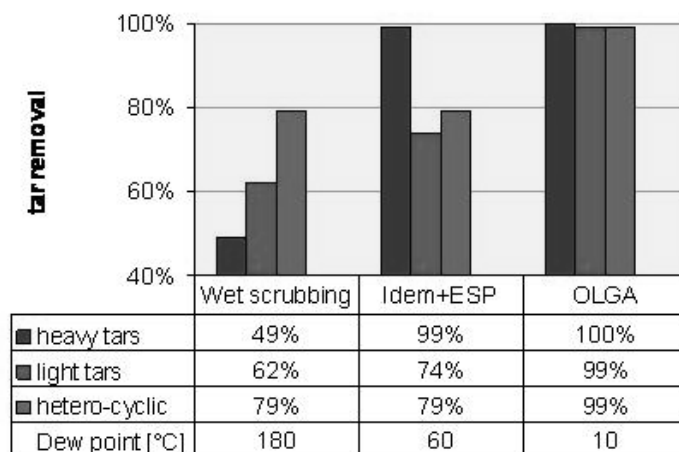|	Wet scrubbing	Idem+ESP	OLGA
■ heavy tars	49%	99%	100%
■ light tars	62%	74%	99%
■ hetero-cyclic	79%	79%	99%
Dew point [°C]	180	60	10

Figure 2-14   *Comparison of scrubbing based tar removal technologies*

In the aqueous scrubber the gas was not on specification for a gas engine. With the addition of a wet ESP the heavy tars were almost completely removed and the tar dew point decreased to 60°C. The producer gas could be applied in a gas engine, but the system suffered from wastewater problems. The OLGA removed the tars almost completely. The tar dew point was reduced well below a temperature of 10°C. The water condensate did not contain phenols and the gas could be applied in a gas engine.

3. Non-tar components

Whereas tar formation is mainly caused by the operating conditions of the gasifier and less by the composition of the biomass feedstock, for non-tar components the situation is reversed. The elemental composition of the feedstock therefore determines the basic requirements for gas cleaning downstream the gasifier.. Table 3.1 shows an indicative composition of several biomass feedstocks taken from the Phyllis database [vi][99], and shows for example that for non-woody biomass, chlorine, sulfur and ash fractions are much higher than for woody biomass. The use of such fuels will therefore most likely require additional gas cleaning measures to overcome either emission problems, corrosion issues or contamination of downstream processes (*i.e.* catalyst deactivation, oil degradation, …).

Table 3.1 *Composition of several biomass feedstocks*

	C (wt%$_{daf}$)	H (wt%$_{daf}$)	O (wt%$_{daf}$)	N (wt%$_{daf}$)	S (wt%$_{daf}$)	Cl (wt%$_{daf}$)	Ash (wt%$_{db}$)	H$_2$O (wt%$_{ar}$)
Untreated wood	48,8	6,0	44,6	0,4	0,03	0,02	1,6	12,8
Treated wood	50,7	6,1	41,7	1,2	0,11	0,08	2,7	17,8
• Demolition	49,4	5,9	43,1	0,9	0,08	0,05	4,3	18,9
• Impregnated	52,5	6,2	40,4	0,6	0,17	0,11	1,5	23,5
• Particle board	50,1	6,2	41,6	2,2	0,08	0,08	2,3	11,1
Grass	49,2	6,0	43,5	0,9	0,16	0,38	3,6	15,4
Straw	50,5	6,1	41,3	1,1	0,15	0,48	10,9	6,1
Manure	51,8	6,4	34,2	4,4	0,85	1,41	32,9	45,7
• Poultry	48,2	5,6	34,8	6,2	0,74	0,73	19,6	30,1
• Cow	53,1	6,8	34,9	2,6	0,95	1,66	43,7	14,9
• Pig	54,1	6,8	33,0	4,3	-	1,84	35,4	92,1
Sludge	50,2	7,2	39,7	2,9	1,00	0,30	25,3	25,3
• Food industry	52,8	8,1	39,9	1,0	0,77	0,01	9,3	7,8
• Paper	49,2	6,0	43,1	1,1	0,45	0,43	33,3	36,8
• Sewage	48,5	7,5	36,2	6,7	1,87	0,53	33,4	31,2
Refuse Derived Fuel	51,8	7,2	39,3	1,1	0,40	0,39	15,0	25,0
Municipal Solid Waste	56,0	5,1	26,6	1,2	0,50	1,13	39,6	34,8

In this chapter, the different gas cleaning technologies for non-tar components are discussed. Also included is a paragraph on unsaturated hydrocarbons still present in the producer gas after tar removal, as these components have a significant influence on downstream synthesis processes, for example on methanation towards Substitute Natural Gas (SNG) [20].
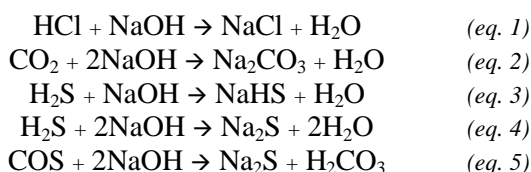
3.1 Chlorine

Chlorine compounds are present in most biomass feedstocks, though sometimes chlorine concentrations are extremely low (table 3.1). When present in combination with ammonia, it can form ammonium chloride (NH$_4$Cl), which at high temperatures is in the vapour phase, but below 250-280°C becomes solid and presents a fouling risk for downstream process steps. When dissolved in (condensed) water it becomes highly corrosive. Similar problems occur in combination with metals present in the feedstock, *e.g.* potassium and sodium. Although not part of the gas cleaning, it is mentioned that chlorine can play a significant role in bed agglomeration issues and that its concentration in the producer gas increases with increasing temperatures of gasification [20].

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vi The Phyllis database: www.phyllis.nl

3.1.1 HCl

HCl removal processes can be categorised in two groups: dry and wet processes [20]. In the dry process, the chlorine is removed with an adsorbent, in the wet process with a scrubbing liquid. For *dry removal* of HCl, two types of adsorbents are commercially available, *i.e.* sodium carbonate (Na_2CO_3, $NaHCO_3$) and calcium oxide (CaO) [56]. For the cleaning of producer gas, CaO is less suitable as it reacts with CO_2. The CO_2 does not influence the performance of Na-sorbents when applied in the temperature range of 300 to 600°C. The optimum temperature for the reaction was found to be between 400 and 500°C [40], at which HCl concentrations in the producer gas can be reduced to below 1 ppmv [99].

The *wet scrubbing* process is usually based on either water or a caustic water solution. The amount of water normally present in the producer gas should be able to remove 500 ppmv of HCl from the gas when condensing. If it is not allowed to dispose the condensate onto surface water, additional water treatment (*e.g.* an ionic exchanger) has to be implemented, which could make the cleaning system rather expensive [99]. The alternative would be to use a caustic scrubber. This will not only remove HCl effectively, but also other components present in the producer gas like CO_2, COS and H_2S [58]. The products formed are all stable salts:

$$HCl + NaOH \rightarrow NaCl + H_2O \qquad (eq.\ 1)$$
$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \qquad (eq.\ 2)$$
$$H_2S + NaOH \rightarrow NaHS + H_2O \qquad (eq.\ 3)$$
$$H_2S + 2NaOH \rightarrow Na_2S + 2H_2O \qquad (eq.\ 4)$$
$$COS + 2NaOH \rightarrow Na_2S + H_2CO_3 \qquad (eq.\ 5)$$

The reaction with CO_2 should be avoided, as the formed carbonate salt has a low solubility. By having limited residence times, this reaction is avoided. The reactions between NaOH and HCl as well as H_2S occur relatively fast; hence it is possible to achieve a high selectivity towards HCl and H_2S while limiting the CO_2 removal from the producer gas [58]. For CO_2 removal a more optimal removal technology may be applied.

3.1.2 Dioxins and furans

Dioxins and furans are emitted in all thermal processes, where the combination of an inadequate process temperature (<850°C), the presence of chlorine as well as insufficient concentration of oxygen and residence time (<2s) allows aromatics to form and/or survive [99]. Dioxins, or officially polychlorinated dibenzodioxins (PCDD, figure 3-1), are a group of poly-halogenated compounds which are significant because they act as highly toxic environmental pollutants.
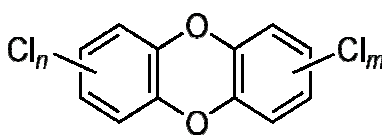

Figure 3-1 *General structure of polychlorinated dibenzodioxins (PCDD)*

Dioxins can be removed from gases through absorption/adsorption in a polymer material. The ADIOX® technology developed by the Forschungszentrum Karlsruhe and Götaverken Miljö uses polypropylene (PP) doped with carbon particles. The process is based on the high affinity of dioxins to carbon - when in contact, the bond between dioxins and carbon is very strong. By dispersing small particles of carbon in PP a dioxin molecule present in the flue gas is first absorbed into the PP, where it migrates to a carbon particle, on which it is very strongly adsorbed (connected to its surface). The plastic material acts as a selective filter with a preference for molecules like dioxin [44].

An alternative for the removal of dioxins is the oil based scrubbing technology OLGA, as discussed in §2.2.7. Duration tests with OLGA for the fuel cell and gas engine application revealed that dioxins were removed together with tars to a sufficiently low level (below 0.1 ng/m³) [99]. Considering the general structure of dioxins (figure 3-1) this does not come as a surprise. The OLGA is designed for cleaning the producer gas, however might be applied for cleaning dioxins from gases as well.

A third alternative for the technology based on carbon adsorption is catalytic destruction of dioxin compounds. For flue gases, this is a commercially available technology. The CRI system for example uses a specially developed catalyst to convert dioxins in the presence of oxygen to a mixture of H_2O, CO_2 and HCl. The specific CRI dioxin destruction catalyst operates at temperatures around $160°$ C [vii]. Dioxin removal straight from the producer gas (with no oxygen present) is not possible with this catalyst.

3.2   Sulfur

The sulfur in the biomass is mainly released as H_2S and COS, and only in small amounts as organic sulfur (mercaptanes and thiophenes). The operating temperature of the gasifier mainly determines the exact ratio between the sulfur components [99]. The organic components, in particular mercaptanes, are unstable at high temperatures, however presence of organic sulfur should not be forgotten as it results in issues in downstream processes (emissions, catalyst deactivation) and often is not removed by conventional H_2S and COS removal technologies. Table 3.2 provides an overview of the pros and cons of different sulfur removal processes. In paragraphs §3.2.1 to 3.2.3 these are discussed in more detail.

Table 3.2   *Pros and cons of sulphur removal processes*

Technology	Pros	Cons	Effect on organic S	Effect on CO_2
Dry sorption / reaction	Limited effect of pressure, wide variety of absorbens available	Waste production, regeneration results in sulphur rich waste gas	Also effective for thiol compounds, unsure for thiophenes	High H_2S selectivity
Physical absorption	Commonly used, solvent regenerable, removes HCN and Hg	High pressures required, removes HC as well, high OPEX	Removes all organic sulphur compounds	Removes also CO_2
Absorption in alkali solution	Relatively simple, commonly used	Corrosion, high heat consumption for regeneration	Partially effective with amines, with K_2CO_3 only traces	High H_2S selectivity, amines however also remove CO_2
Liquid oxidation	Results in elementary sulphur	Large equipment, low quality sulphur	Also effective for thiols, not for COS	High H_2S selectivity
Adsorption		Regeneration results in sulphur rich waste gas	Also effective for some organic sulphur compounds	High H_2S selectivity, can however also remove CO_2
Biological removal	Mild conditions, limited CAPEX	Functionality unsure for HC containing gas	Unknown	High H_2S selectivity

3.2.1 H_2S

The removal of H_2S is often coupled to CO_2 removal. Kohl [58] gives general guidelines for a preliminary screening for a H_2S and CO_2 removal process, grouping the H_2S removal processes into six types. Table 3.3 gives the list and also suggests the preferred areas of application for each process type. This is particular of interest as conventional H_2S removal technologies might be less interesting for H_2S removal from biomass based producer gases due to the relatively small amount of H_2S present.

Table 3.3   *Guideline for H_2S removal processes*

	Plant size	Partial pressure	Sulfur removal capacity
Absorption in alkali solution	> 25,000 m_n^3/h	< 7 bara	> 10 ton/day
Physical absorption	> 25,000 m_n^3/h	> 7 bara	> 10 ton/day
Liquid oxidation	> 25,000 m_n^3/h	< 7 bara	< 10 ton/day
Dry sorption / reaction	< 25,000 m_n^3/h	< 7 bara	< 10 ton/day
Adsorption	< 25,000 m_n^3/h	< 7 bara	< 10 ton/day
Membrane permeation	< 25,000 m_n^3/h	> 7 bara	< 10 ton/day

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vii CRI catalysts: www.cricatalyst.com

Both absorption in an alkaline solution (chemisorption by e. g. aqueous diethanolamine, NaOH solution) and in a physical sorbent (*e.g.* poly ethylene glycol) are suitable for treating high-volume gas streams containing H_2S and/or CO_2 to below 1 ppmv. However, physical absorption processes are not economically competitive when the partial pressure is low as the capacity of physical solvents is a strong function of partial pressure [99]. The boundary line between physical and chemical solvents is approximately 7 bara [90].

Solid sorption is applicable to low quantities of H_2S. Suitable adsorbents are oxides of Fe (~1 ppmv), Mn (~5), Zn (<0.3), Cu (<1) and Ca (~50), with the final H_2S concentration achievable reported between brackets. Operating temperatures are between 350 and 500°C, except for Ca and Mn (up to 1000°C). Most sorbents cannot be regenerated and must be disposed after being used, although regenerative processes are under development. Adsorption with molecular sieves is a viable option when the amount of sulfur is very low and the gas contains heavier S compounds (such as mercaptane and COS) that must also be removed [99]. The effect on thiophenes, however, is limited.

Membrane permeation involves the separation of individual compounds on the basis of the difference in their rates of permeation through a thin membrane barrier. In general membranes for H_2S removal (< 1ppmv) are applied for small-scale plants with gases containing a high H_2S concentration. The capacity is accomplished by using proportionately increasing number of modules. Therefore, the process does not realize the economy of scale and becomes economically less competitive with absorption processes as the plant size is increased [99].

In general H_2S can be recovered as elemental sulfur, S, by using a biological process or by the reaction with SO_x [99]. The standard technology for recovery of concentrated H_2S to elemental sulfur is the Claus process. Normally this process is operated parallel to physical or chemical absorption/desorption process like the Rectisol process or alkanol amine processes. The Rectisol or alkaline amine process removes the H_2S from a diluted gas stream. The gas from the desorption step is concentrated with H_2S and can be applied in the Claus process for the conversion of H_2S to elemental sulfur. In general the Claus process will be too expensive on the small scales associated to biomass applications. Even for large scale biomass gasification facilities the amounts of sulfur are limited, unless typical feedstocks like MSW, RDF, manure or sludge are applied. Alternatively to the Claus process, H_2S can be easily and economically converted to elemental sulfur by biological processes, using microorganism to convert S^{2-} to elemental S. The H_2S can be removed in an alkaline scrubber from the gas. The chemically absorbed H_2S can consequently be fed to the biological reactor where the H_2S in the solution is converted into elemental sulfur with the bacteria present in the reactor. The THIOPAQ process by Paques [viii] is an example of such a biological process.

3.2.2 COS

Carbonyl sulphide (COS) is an organic sulfur compound, that can not be removed efficiently by physical or chemical removal processes. Thermodynamically, COS will shift towards formation of H_2S though as the gas is cooled down to a low temperature. At a gas temperature of 200 °C, thermodynamically there is no COS present. This implies that it is possible to convert COS to H_2S. Catalysts applied for this conversion include activated alumina, titania on alumina and Mo/Co catalyst. The ZnS product from the absorption of H_2S with ZnO also catalyzes the COS conversion via the hydrogenation reaction. So, when the ZnO bed contains ZnS, COS can be converted into H_2S, which is, subsequently, adsorbed by the ZnO. As such, an upstream catalyst for the removal of COS would not be necessary [99].
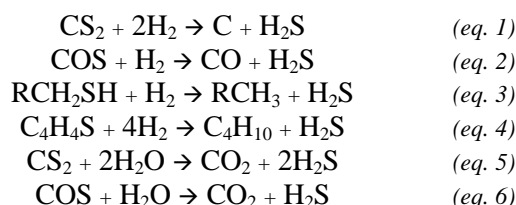
3.2.3 Other organic sulphur compounds

The principal organic sulfur compounds that are present in the producer gas are carbonyl sulfide (COS, §3.2.2), carbon disulfide (CS_2), mercaptans (RSH), thiols (CH_4S, C_2H_5SH), thiophenols (C_6H_6S), and thiophenes (aromatic sulfur, *e.g.* C_4H_4S). The organic sulfur compounds are much less acidic than hydrogen sulfide (H_2S) and are therefore not effectively removed by conventional alkaline solution based H_2S removal technologies. Physical solvents, however, generally show a very high solubility for organic

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[viii] The THIOPAQ process by Paques: www.paques.nl

sulfur compounds [58]. The absorbed organic sulfur compounds end up in the separated acid gas stream. Although effective for contaminant removal, these physical solvents often also remove considerable amounts of valuable hydrocarbons, among which also (small) amounts of CH_4. As such, they are often not preferred.

For high-efficient processes, *e.g.* the synthesis of ammonia, substitute natural gas, methanol, and other chemicals, catalytic conversion of the organic sulfur compounds is more interesting [58]. In catalytic conversion, the organic sulfur is hydrodesulfurized upstream the H_2S removal into H_2S via either hydrogenation (*e.g.* equation 1 to 4) or hydrolysis (*e.g.* equation 5 and 6):

$$CS_2 + 2H_2 \rightarrow C + H_2S \qquad \textit{(eq. 1)}$$
$$COS + H_2 \rightarrow CO + H_2S \qquad \textit{(eq. 2)}$$
$$RCH_2SH + H_2 \rightarrow RCH_3 + H_2S \qquad \textit{(eq. 3)}$$
$$C_4H_4S + 4H_2 \rightarrow C_4H_{10} + H_2S \qquad \textit{(eq. 4)}$$
$$CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S \qquad \textit{(eq. 5)}$$
$$COS + H_2O \rightarrow CO_2 + H_2S \qquad \textit{(eq. 6)}$$

The first hydrogenation reaction (equation 1) demonstrates the risk of carbon formation. The first catalysts used commercially for hydrodesulfurisation at the beginning of 1900 were based on nickel sulfide catalysts, followed in the mid 1900's by copper, iron, zinc, cobalt, or nickel thiomolybdates. All were operated at temperatures between 300 and 450°C. Due to the deposition of carbon the catalysts have to be regenerated on a regular basis [58].

Nowadays, most hydrodesulfurisation (HDS) catalysts are based on cobalt and nickel and molybdenum oxides on an active (possibly titanium enhanced) alumina base (Al-Co-Mo and Al-Ni-Mo). These catalysts are effective at decreased volumes of catalyst charges as well as at sudden change of sulfur content and are operated at temperatures between 250 and 400°C and at elevated pressure (up to 40 bar). Prior to use, the oxidised catalyst has to be sulfided [58], as the active phase in the operating catalyst is the Co-Mo-S or Ni-Mo-S phase. This sulfidation will normally take place by exposing the catalyst as delivered to the normal operating conditions in the plant, *i.e.* the sulfur for sulfidation is supplied by the feed and at the concentration at which it is available [85]. The CoMo and NiMo catalysts are mainly developed for fossil based technologies and are commercially available from the leading catalyst suppliers such as Haldor Topsøe, Süd Chemie and Johnson Matthey. Application of these catalysts for biomass based processes, as done by ECN [20][74][104][105] and PSI [14][15][16] in their SNG development, might cause some issues concerning the sulfur and olefins concentrations in the producer gas and the relatively low operating pressures.

If the *sulfur* content in the feed is constant and low, the stable sulfur concentration in the catalyst and thus the activity will be low. Although normally not problematic, the catalyst may not convert organic sulfur sufficiently during a short period if the concentration suddenly increases. The catalyst will have to be fully sulfided before the slip of organic sulfur will go down again [85]. If the *olefins* are hydrogenated as well, this exothermic reaction will cause a significant temperature increase over the HDS reactor. As such, it might be necessary to lower the inlet temperature of the HDS reactor; however this will have a negative effect on the HDS of the organic sulfur compounds [58]. The *low operating pressures* compared to the normal operating conditions for which the HDS catalysts are designed (10 and 40 bar) also has a significant influence on the HDS catalyst activity. Experiments with a $Ni-Mo/SiO_2$ catalyst at different temperatures and partial pressures showed a significant effect of both parameters on the catalytic activity, as is illustrated in figure 3-2 [21][106].
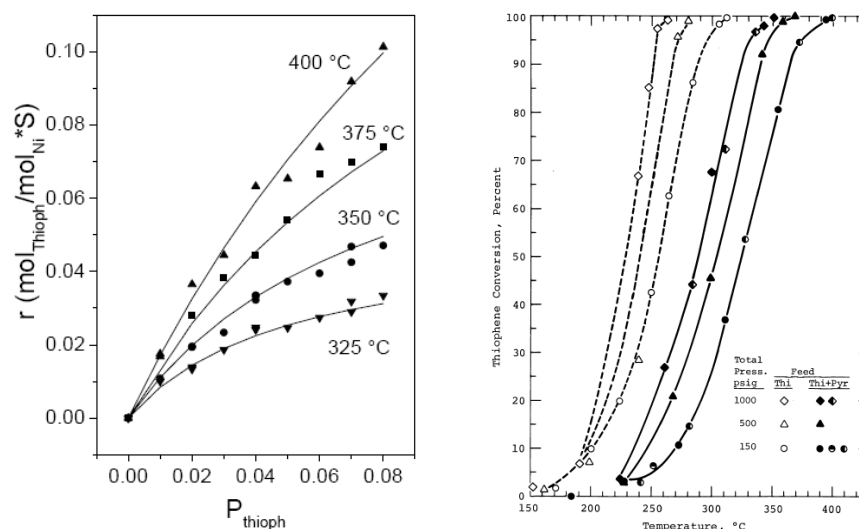
Figure 3-2 *Catalytic activity for thiophene HDS versus thiophene (partial) pressure*

3.3 Nitrogen

Nitrogen present in the producer gas originates either from the feedstock (typically ending up in the form of HCN and NH_3, partially as pyridine, in the producer gas) or from the gasifying agent (in the form of N_2 in case of air-blown gasification, HCN and NH_3 resulting from molecular nitrogen can be neglected) [47]. Compared to coal based gasification, the HCN concentrations in the biomass producer gas are roughly the same (~20 ppmv), the NH_3 concentration, however, can be significantly higher (up to thousands of ppmv compared to up to 40 ppmv for coal) [17][47].

The presence of NH_3 as well as chlorine in the producer gas might result in the formation of NH_4Cl, a chemical that becomes solid below 250-280°C and presents a fouling risk [47]. Ammonia in the presence of H_2S can result in formation of ammonium(poly)sulphide, which solidifies at temperatures below 150°C. HCN is reported to be a potential contributor to the deactivation of for example FT catalysts [17]. When hot producer gas is used to generate electricity in integrated gasification combined cycle (IGCC) power plants, both NH_3 and HCN will partly be converted to nitrogen oxides (NO_x) which are difficult to remove and are highly undesirable as atmospheric pollutants. Removal of NH_3 and HCN is therefore often required.

For NH_3 removal either catalytic destruction or wet scrubbing can be applied. Catalytic destruction of NH_3 is possible using catalysts similar to those used for tar cracking or hydrocarbon reforming. Dolomite, Ni-based steam reforming catalysts as well as Fe-based catalysts have all been reported to be able to convert NH_3 at temperatures of approximately 900°C [63][64][83]. Using these catalysts, destruction of >99% of the NH_3 is possible [84]. Although this combined tar and NH_3 removal has the potential to remove both tars and NH_3 from the producer gas while maintaining the heat of the producer gas, commercial tar cracking systems at this temperature are still under development (§2.1.3).

Ammonia may also be removed from the producer gas by wet scrubbing. The main problem with wet scrubbing is the presence of tars in the producer gas, which end up in the water as well. At the Harboøre plant the tar and NH_3 contaminated waste water is treated in the tar water cleaning system (TARWATC) [76] (§2.2.5). More ideally tars and NH_3 are removed separately in order to avoid contamination of the water with tars. However, this requires the removal of tar before the wet scrubber to such a level that the tar dew point is well below the operating temperature of the water scrubber, *i.e.* well below approximately 30°C. The oil scrubbing technology OLGA (§2.2.7) is capable of doing this and therefore allows downstream implementation of a "conventional" water scrubbing system [59]. The NH_3 is soluble in water and can either be neutralised with acids to form ammonia salts, converted biologically into N_2 or stripped from the scrubbing water.

In the latter case, the stripper air containing the NH_3 can be recycled to the gasifier to be converted to N_2 and H_2O. This conversion requires a temperature above 800°C in order to reach over 50% conversion and is nearly complete (>90%) at 850°C [72]. The presence of oxygen or air at the injection point will lead to a much higher rate of NH_3 destruction than observed for pure thermal cracking. Tests at ECN also revealed hardly any NH_3 was converted to NO_x.

When applying a biological process to clean the scrubbing water, *e.g.* via the ANAMMOX® process, bacteria convert NH_3 into N_2 via a combination of nitrification and de-nitrification reactions (figure 3-3). In 2002 the first full-scale plant was started up in the Netherlands and at this moment four installations are operational [ix].The process can be used for the removal of ammonium with a relatively high ammonium concentration (>100 mg/l), however the bacteria's applied are sensitive for hydrocarbon pollution.
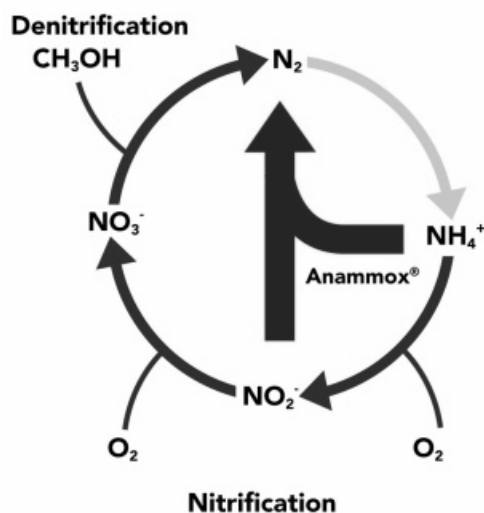

Figure 3-3 *Biological ammonia removal*

3.4 Carbon dioxide

Removal of CO_2 from the producer gas may be necessary for various reasons. In combination with water, it is for example highly corrosive and rapidly destroys pipelines and equipment unless it is partially removed or exotic and expensive construction materials are used. Furthermore, for specific processes like methanol and FT diesel synthesis the inert CO_2 present in the gas will require higher overall operating pressures. Within the framework of the EOS-LT consortium project "Biomass gasification and gas cleaning" though, the removal of CO_2 is mainly done for the purpose of producing (substitute natural) gas with a high enough heating value to comply with the standards of the conventional application of the gas and (to a lesser extent) the purpose of carbon capture and storage (CCS).

For CO_2 removal a wide variety of technologies are commercially available, including conventional absorption processes, such as the Benfield^{TM} process based on hot potassium carbonate solutions and amine scrubbing processes based on formulated solvents (*e.g.* MEA, DEA, MDEA [x]). However, also cryogenic as well as adsorption processes (*e.g.* PSA, TSA [xi]) and membranes are commercially available. For a detailed description of all these CO_2 removing technologies reference is made to the *Gas purification* handbook by Kohl and Nielsen [58].

In the status report at hand, the focus for CO_2 removal is on upgrading the quality of the producer gas. This is comparable with the upgrading of biogas or landfill gas. Overviews of these existing upgrading technologies by André de Boer and Mathieu Dumont of SenterNovem [34][39] are included in chapter 4 of this status report. Possible issues when applying these conventional upgrading technologies in thermo-chemical systems are provided in chapter 4 as well.

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ix The Paques ANAMMOX process: www.paques.nl
x   MEA = Mono Ethanol Amine; DEA = Di Ethanol Amine; MDEA = Methyl Di Ethanol Amine
xi PSA = Pressure Swing Adsorption; TSA = Thermal Swing Adsorption

3.5 Unsaturated hydrocarbons

The existence of unsaturated hydrocarbons in the producer gas varies widely and does not only include tars for which the removal technologies are described in chapter 2 [xii], but also light unsaturated hydrocarbons like acetylene (C_2H_2), ethylene (C_2H_4) and benzene (C_6H_6). Unlike tars, these components do not create a high fouling risk due to straight condensation. However, they can react with and deactivate synthesis catalysts through carbon deposition or form gummy polymers that subsequently can plug downstream equipment due to condensation. The removal of unsaturated hydrocarbons can be done via physical separation (*e.g.* amine scrubbing, though with regards to selectivity cryogenics or selective adsorption makes more sense). Selective catalytic hydrogenation is however usually the preferred technique [58].

Platinum or palladium based catalysts typically can be used for the hydrogenation of C_2H_2 and C_2H_4 at relatively low temperatures. The NiMo and CoMo catalysts applied for HDS (§3.2.3) also demonstrated hydrogenation activity for unsaturated hydrocarbons and are unlike the Pt or Pd catalysts not sensitive for sulfur deactivation. From the hydrocarbon composition before and after the HDS it is clear that the compounds are actually hydrogenated towards CH_4 and C_2H_6, and not cracked into CO and H_2 [20] . Experiments at PSI, however, also reveal that even after HDS not all unsaturated hydrocarbons are removed from the gas [13]. The components still present (*i.e.* C_3H_6, as well as C_6H_6 and C_7H_8 not completely removed in the tar removal step [20]) cause a significant risk of soot formation on the methanation catalysts applied at ECN and PSI [13][20]. When using a fluid bed methanation process, this soot formation might not be problematic and the catalyst might continuously be regenerated.

R&D on removal of these components via scrubbing, hydrogenation or reforming is ongoing [13][20][86] and is crucial for long-term operation of catalytic synthesis processes downstream tar producing gasifiers. Although conventional (amine or methanol based) scrubbing technology [xiii] can easily solve this specific problem, severe scrubbing of the producer gas is not considered to be economically attractive due to the efficiency penalty associated with it and the complexity of cleaning the scrubbing medium. Maintaining the hydrocarbons in the producer gas, either as (stable) saturated light hydrocarbons (*i.e.* CH_4 or even better C_2H_6 and C_3H_8) or if necessary converted to synthesis intermediates (*i.e.* CO and H_2), will result in significantly higher production efficiencies, and hence ultimately an economically more attractive process.

3.6 Particles and alkalis

The need for particulate and alkali removal significantly depends on the use of the producer gas. For gas engines, particulate levels must be reduced to below 50 mg/m_n^3, whereas for turbines (< 15 mg/m_n^3) and catalytic processes (<0.02 mg/m_n^3) the requirements are even more stringent [84]. These particulates do not only include char and ash present in the initial producer gas of the gasifier, but also alkalis. The mineral matter in biomass contains high levels of alkali salts, particularly *e.g.* grass, straw and other fast growing biomass, which contain large amounts of potassium. At temperatures of around 800°C, the alkali salts can vaporize and create problems by depositing on cooler surfaces downstream. The alkali will remain in the vapour phase until it condenses due to cooling below about 650°C, typically forming small particulates (<5 µm) or condensing straight on surrounding surfaces like other particulates or the process equipment. In gasification, alkali vapours are removed by cooling the hot producer gas below 600°C to allow for condensation of the material into solid particulates [84]. The solids are then removed using various dry or wet particle removal systems. These particle removal systems not only have to be designed taking into account the chemical behaviour of the condensed alkali salt, but also the effect of tar condensation (appendix A). As such, particle removal is normally closely linked to and installed together with some kind of tar removal technology, as became already clear in §2.1 and 2.2 of the status report at hand. In this paragraph, the main particle removal technologies are discussed briefly, emphasising in particular on the issues that occur when applying these "conventional" technologies in a tar loaded producer gas stream.

[xii] A well accepted definition states that tars are all organic compounds with a molecular weight higher than benzene. A better and more detailed tar description is given by the classification of tars as described in appendices A and B.

[xiii] Process like the methanol based Rectisol® process or alkanol amine processes are known for their combined removal of sulphur, nitrogen and hydrocarbon contaminants however are hardly selective and require significant stripping and/or distillation to regenerate the scrubbing medium applied.

3.6.1 Cyclones

In a cyclone, the particles containing producer gas is introduced tangentially into a cylinder. The gas exits the cyclone at the top while the particles, separated from the gas via centrifugal forces, slide along the wall of the cylinder to a dust collection chamber at the bottom of the cyclone (figure 3-4) [24]. Cyclones are particularly effective (>90%) at removing particles larger than a few micrometers with minimum pressure drop [84]. Smaller particles however are not caught.
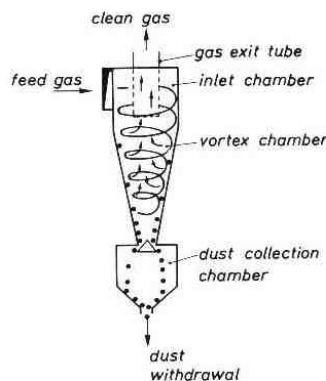

Figure 3-4 *The mechanical principle of a cyclone*

Cyclones are commonly used, also in biomass gasification systems, and are commercially available from many vendors. Typically they are operated at high temperature to avoid condensation of tars in the cyclone and often they are used as multiple units in series. A circulating fluidised bed gasifier will in general have an initial cyclone operated at the temperature of the gasifier, in which the bulk of unconverted char and ash is separated from the producer gas in order to be circulated to the bottom of the gasifier. Downstream this cyclone, multiple (colder) cyclones can be placed to collect particles with different sizes as well.

The positioning of a cyclone in a gasification system can determine the success of the system. Due to the particle vortex it is possible to operate a cyclone at temperatures (slightly) below the tar dewpoint; the particles can remove some condensed tars from the walls as long as condensation is not too significant. Without the presence of these particles, the cyclone will not be cleaned. For this reason it is also recommended not to position a (final) cyclone upstream gas coolers, as in that case no particles are present capable of removing tars in the difficult producer gas cooling step as well.

3.6.2 Barrier filters

Barrier filters are based on porous materials (*e.g.* metal or ceramic candles, bag filters, packed bed filters) that allow gases to pass, while blocking the particles (figure 3-4). They effectively remove small-diameter particulates in the range of 0.5 to 100 μm. Removal of smaller particles is also possible though associated with high pressure drops over the filters. The particles can be removed from the filter material by periodically pulsing clean gas through the filter in the reverse direction of normal gas flow [24]. To reduce the overall particulate load, these filters are typically placed downstream cyclones.
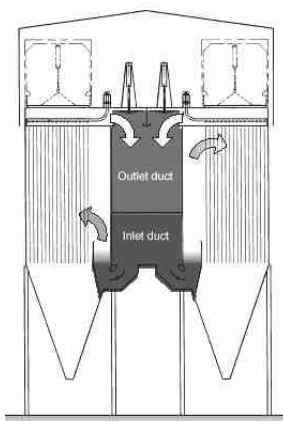

Figure 3-5 *The mechanical principle of a barrier filter*

Although barrier filters are effective for removing dry particulates, they are less suitable for wet or sticky contaminants such as tars. Tars cling to the filter surface and can undergo subsequent carbonization reactions that lead to fouling and plugging [24]. Hence, in biomass producer gases, these barrier filters are applied either in gases where tars are already significantly removed (*e.g.* at Güssing, §2.1.3.1 and Skive, §2.1.3.2) or operated at high temperature, above the dewpoint of tar.

These high temperature gas filters (HGF) were tested at the commercial demonstration facility at Värnamo, Sweden [88] and more recently at the pilot facility at ECN [101]. At both sites, the filters were operated at 350 to 400°C, hence above the tar dewpoint. At Värnamo, the ceramic candle elements broke repeatedly due to the frequent thermal cycling in the demonstration facility that operated intermittently [24]. This has been solved by using metal fibre filters. The tests at ECN were not successful. Fouling of the HGF upstream the OLGA tar removal led to a serious increase of the pressure drop over the HGF (Figure 3-6). The HGF upstream the OLGA system was successfully replaced by an electrostatic precipitator within OLGA (§2.2.7).
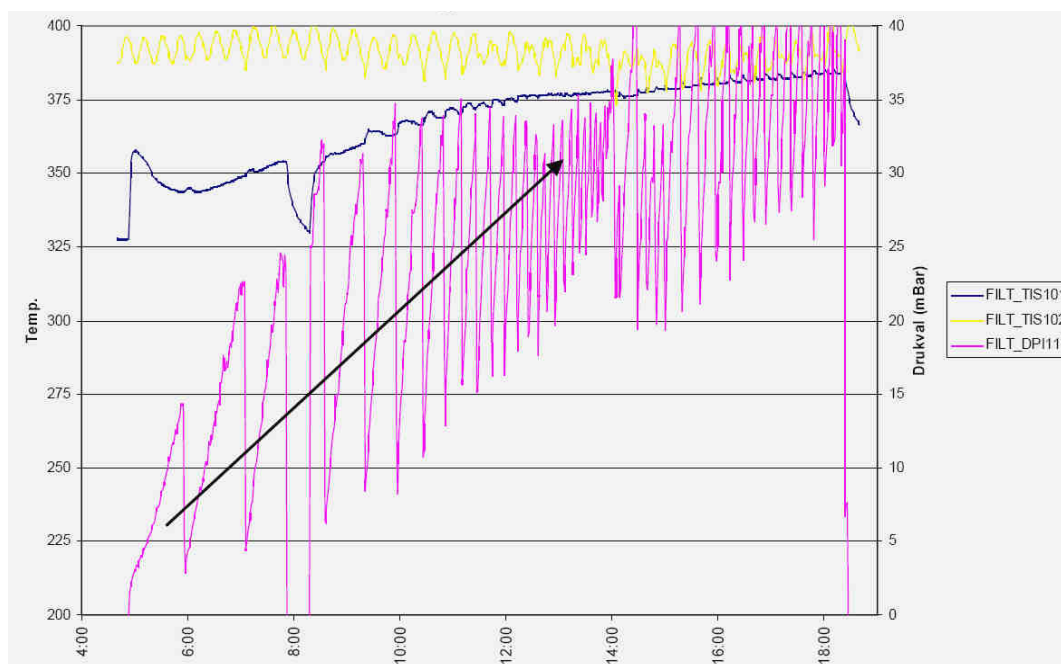

Figure 3-6 *Temperature (blue line) and pressure drop (pink line) of the hot gas filter at ECN*

HGF research now mainly focuses on the combined ceramic gas filtration and catalytic tar cracking [45] as being developed by Pall (Schumacher) and Madison Filter (in cooperation with Haldor Topsøe) as discussed in §2.1.3.3. These filters operate at temperatures of around 750 to 900°C, and as a result are relatively large and expensive units. Operation of barrier filters at lower temperatures however often resulted in tar fouling, hence making the filters only applicable downstream some kind of tar removal unit or downstream gasifiers with an initially low tar dewpoint.

3.6.3 Electrostatic filters / scrubbing technology

Electrostatic filters are based on separating charged particles in an electrostatic field. The particles are collected on so called plate curtains (figure 3-7), where the formed particle layer is removed via dry or wet methods [24]. The dry methods are based on mechanical cleaning of the surface area and can operate at high temperatures (up to 500°C), whereas in wet methods the particle layer is removed with a thin film of flowing liquid, usually water. As such the wet ESP has a typical operating temperature below 100°C, or at least below the condensation temperature of the liquid applied. With the ESP being relatively expensive on a small scale, the technology is attractive only for large-scale operation [84].
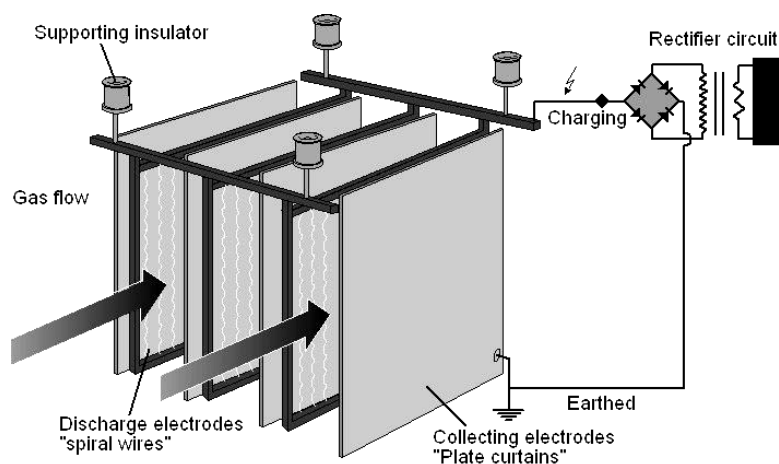
Figure 3-7 *The mechanical principle of an electrostatic filter*

As good charging of particles would require a minimal particle size of 0.5 μm, an ESP is in general less efficient for small particles. Often though, ESP systems are applied downstream a cooling and scrubbing system, in which small particles present in the gas (*e.g.* ash, aerosols) grow in particle size due to condensation of a liquid on the particle, being either water, RME or oil. As such, an ESP becomes suitable as well for small particles and hence very high separation efficiencies can be obtained.

The ESP has been applied successfully in several biomass gasification systems and has therefore become a commercially proven and available technology for thermal biomass conversion systems as well. The issues with tar are dealt with by having a scrubber installed upstream the ESP. At Harboøre (§2.2.5), the particles (including tar aerosols) grow by condensation of water on the particle and as such are separated in a water based wet ESP. In the RME (§2.2.6) as well as the oil based OLGA (§2.2.7) scrubbing technology the principle is the same, however in stead of water, RME or oil is used. As such, the (wet) ESP not only operates as a filter for particles (e.g. ash, dust, alkalis), but also as a tar aerosol filter.

4. Biogas upgrading technologies

Although upgrading of biogas or landfill gas is not considered to be a R&D topic within the EOS research area "gasification, gas cleaning, conditioning and syngas production", an overview of these existing upgrading technologies by André de Boer of SenterNovem [34] is included in this chapter, and formed the basis of a leaflet by Mathieu Dumont of SenterNovem [39]. The technologies in this sector may also apply for gas obtained from thermo-chemical conversion processes, in particular when aiming for the production of SNG.

Due to the differences between thermo-chemical and bio-chemical processes, some comments on possible issues when applying these conventional upgrading technologies in thermo-chemical systems are included at the end of this chapter.

4.1 Conventional upgrading technologies

The new trend in biogas production is the upgrading of the biogas to natural gas quality and injecting this upgraded biogas in the natural gas distribution grid. Five existing upgrading technologies currently exist on a commercial basis. This memo tries to provide a comparative overview of these five technologies.

Vacuum Pressure Swing Adsorption
This batch-wise operated process uses activated carbon molecular sieves to filter the pressurised biogas. The sieves mainly adsorb CO_2, while letting the CH_4 pass. The coal is regenerated by lowing the pressure to levels well below 1 bara. In these vacuum conditions the CO_2 is released and the carbon can be used again for CO_2 adsorbtion at elevated pressure.

Membranes
In this continues process compressed biogas flows through a membrane with high selectivity for CO_2 and low selectivity for CH_4. As a result, two gas streams are obtained, one containing the CO_2 and the other the CH_4. Due to limitations in the membrane selectivity both streams are slightly contaminated by the other component.

Water wash
In this continues process, the biogas flows though circulated cold water, dissolving hardly any CH_4 though significant amounts of CO_2. The remaining gas however still contains some CO_2. The CO_2 is removed from the saturated water at elevated temperatures. After re-cooling, the water can be used again.

LP Cooab
This continues low-pressure CO_2 absorption process operates in a similar way as the water wash process. In stead of water, an amine solution is used though with higher CO_2 and lower CH_4 absorption performance. As a result, the separation of CO_2 from CH_4 is significantly improved.

Cryogenic
This process can be operated both batch-wise and continuously. The biogas is cooled to temperatures at which the CO_2 becomes liquid, while the CH_4 is still present in a gaseous phase. The easily separated CO_2 is sold either as liquid or re-vaporised after which it might be injected in CO_2 grids.

For biogas upgrading technologies, the following parameters play a crucial role:

> *Electric efficiency:* The electric efficiency is mainly influenced by the required compression steps (if applicable). A smart design can reduce the overall electricity consumption of compression and decompression significantly.
> *Thermal efficiency:* The thermal efficiency is mainly influenced by the required heat for the recovery of the absorbent or the adsorbent and the heating after adiabatic expansion.

> *Energetic efficiency:* The energetic efficiency is a combination of both electric and thermal efficiency, and is based on the assumption that the required process energy is generated by the initial biogas.

> *Methane slip:* CH_4 is inevitably partially removed from the biogas as well together with the undesired components like CO_2. This GHG CH_4 hence ends up in the waste gas stream or even worse is vented off. In the later case, the negative effect of methane slip might be limited by sending this gas to the air-inlet of a CHP plant (if applicable).

In table 4.1 some characteristics of conventional biogas upgrading technologies are listed. The figures presented are all base don upgrading 1 mn³ biogas with initial methane content of 65% and on injection of the upgraded biogas in a natural gas grid operated at 4bara.

Table 4.1 *Characteristics of conventional biogas upgrading technologies*

	VPSA	Membrane	Water wash	LP Cooab	Cryogen
Operating pressure [xiv]	~5 bar	> 8 bar	> 8 bar	~ 8 bar	10-18 bar [39]
Energy consumption					
- electric (kWh_e) [xv]	0.25	0.14	0.40	0.12	~0.22
- thermal (kW_{th}) [xvi]	0	0	0	0.4	0.04
- methane slip (%)	3%	18%	3%	0.1%	Limited
Simplified efficiency [xvii]					
- without heat recovery (%)	93	80	91	92	~95
-with heat recovery (%)	93	96	91	98	~96
Methane in final gas [39]	max. 98%	max. 90%	max. 98%	max. 99.5%	max. 99.5%

4.2   Issues in relation to thermo-chemical systems

It has to be mentioned that possible issues exist when applying these conventional upgrading technologies in thermo-chemical systems. In general, the final SNG will have a similar composition compared to biogas, though the pressure level at the end is much higher due to the methanation at an elevated pressure. This will influence the presented figures significantly. For example, the low pressure LP Cooab process would make less sense, as the inlet pressure of this process is near atmospheric.

Within the thermo-chemical SNG production the CO_2 removal might however also be placed more upstream in the process, where pressure levels are still relatively low, even near atmospheric. This will also influence the presented figures significantly. In that case, the low pressure LP Cooab process would make more sense, as it is the only process benefitting from a low initial pressure. A final more general comment is that for most biogas plants, low value residual heat is not at hand, hence upgrading technologies with low thermal energy consumption might be preferred (*i.e.* VPSA, membranes and water washes). In a thermo-chemical SNG production process significant amounts of low value residual heat are available, hence upgrading technologies with high thermal energy consumption might be acceptable and the focus would be on reducing the electric energy consumption (*i.e.* LP Cooab).

[xiv] Highest pressure level reached within the system

[xv] Electric energy as required from the grid, note that the primary energy requirement is 2.5 times the presented figure

[xvi] Thermal energy as required, note that this can often be obtained from low value heat as it is associated with recovery of the absorbens (LP Cooab) or re-heating after severe cooling (cryogene)

[xvii] Ratio between the amount of gas energy injected in the grid and the original energy in the initial biogas

5. Conclusions and recommendations

Gasification of biomass results in a producer gas containing numerous contaminants like dust, tar, (organic) sulfur, nitrogen and chlorine compounds, as well as alkali and heavy metals. Although concentrations could be relatively low depending on the feedstock used and the type of gasifier applied, at least some of these contaminants have to be destructed or removed upstream the final application of the producer gas, whether it is a boiler, gas engine or turbine, fuel cell or synthetic application. Hence, gas cleaning in general is inevitable.

5.1 Conclusions

Still not many gasifiers are operating commercially on biomass feedstock, in particular when not taking into account those gasification systems (co-)firing the product straight into boilers. The need for gas cleaning, and in particular tar removal technology, for CHP or synthesis purposes is the Achilles heel of biomass gasification [57]. Standard technology has proven to be insufficient for tar destruction or removal and led to years of RD&D on thermal and catalytic tar cracking as well as (advanced) scrubbing technologies. For the moment, the latter ones seem to have made the biggest progress, with operating biomass based CHP plants at *e.g.* Harbøre and Güssing, and water as well as organic liquid (RME, oil) based technologies being commercially available.

Similar to tar removal technology, standard commercially available technology for removal of non-tar components up to now has also proven to be insufficient, in particular for critical applications of the producer gas in fuel cells or chemical synthesis. Part of that has to do with upstream tar removal being either insufficient (*i.e.* to low efficiencies of the tar removal) or not designed for the more stringent producer gas specifications for these applications (*i.e.* trace tar components still present in the gas). Another part of that is caused by the presence of gas contaminants previously not considered problematic for CHP applications (*e.g.* organic sulfur, dioxins). As can be expected, the biggest progress towards integrated gas cleaning for non-tar components is made by those who are skilful at tar removal as well.

One of the lessons learned in RD&D of gas cleaning is that conventional technology is not always applicable as such in thermo chemical conversion of biomass. Not only will producer gas always contain unfamiliar (trace) components, also in many cases operating conditions like temperature and in particular pressure will be different from the conventional operating conditions of the technology just because it is not (yet) possible to operate the thermo chemical conversion process at these conditions.

For that reason, it makes sense to test conventional technology first on realistic "biomass based" gases and conditions before installing them on large scale. It could be that due to the different gases and conditions (for the moment) thermo chemical biomass conversion systems need different technologies than bio chemical conversion systems or even thermo chemical coal conversion systems.

5.2 R&D issues left

Over the years there has been a tendency for biomass gasification and gas cleaning to apply conventional technology or mimic coal gasification systems. For the gasification process this philosophy already mostly has been dropped. Also the need for pressurised biomass gasification seems to be more or less abandoned or at least postponed, argued by the complexity of biomass feeding. All commercially operating biomass based gasifiers operate at (near) atmospheric pressure, not at the pressure levels of 30 bars and higher, that are typical for coal and oil based gasifiers. Concerning gas cleaning, whether it is removal of tars or non-tar components, the operating conditions for commercially available conventional technology will differ significantly from the conditions downstream a biomass gasifier. Hence, the feasibility of conventional technology will have to be reconsidred or at least test it in realistic conditions. It might well be that conventional technology is not suitable for biomass based processes.

Furthermore, a step by step approach is advised in which technology is scaled up gradually. There has been a tendency to construct large (demonstration) facilities hoping that these are operated successfully and due to scale are commercially attractive as well. The risks are high though, as solving unexpected issues will require enormous budgets. The risk that such a plant becomes mothballed instead of a commercial success has been proven to be relevant. Examples of this are the 180 ton per day Battelle gasification plant in Burlington, USA, and the 8 MW_e ARBRE combined-cycle plant in Eggborough, UK.

The step by step approach becomes even more important for systems with multiple process steps, e.g. biomass gasification based synthesis systems like the production of Substitute Natural Gas (SNG), DME and Fischer-Tropsch (FT) diesel. In these processes focus is not only required on the two main process steps of gasification and tar removal, but also on further gas cleaning (e.g. the removal of organic sulphur, unsaturated hydrocarbons, chlorine and ammonia) and the continuous long-term operation of synthesis units that often are not able to handle even small amounts of trace contaminants [107].

For the successful development of these complex systems, slipstream testing of the critical catalytic components in gas cleaning and synthesis in an upscaled (demonstration) CHP plant consisting of the upstream gasifier and tar removal could benefit the RD&D of the whole system [107], as it enables long duration tests with the critical components under realistic gas conditions.

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Appendix A Tar definition and related issues

A.1 Definition of tars

The presence of tars in the producer gas is a big problem in the commercial utilisation of biomass producer gas as source of sustainable energy. Tar is formed in the gasifier and comprises a wide spectrum of organic compounds, generally consisting of several aromatic rings. A well accepted definition states that tars are all organic compounds with a molecular weight higher than benzene. A better and more detailed tar description is given by the classification of tars (table A.1, more detailed information on individual tar components is given in appendix B).

Table A.1 *Description of the tar classes with a focus on the tar properties and typical components*

Class 1	*GC undetectable tars:* This class includes the heaviest tars that condense at high temperature even at very low concentrations.	gravimetric tars
Class 2	*Heterocyclic components:* These are components that generally exhibit high water solubility, due to their polarity.	pyridine, phenol, cresol, quinoline
Class 3	*Aromatic components:* Light hydrocarbons that are not important in condensation, however might cause issues concerning their solubility in water	xylene, styrene, toluene
Class 4	*Light polyaromatic hydrocarbons (2-3 rings PAH's):* These components condense at relatively high concentrations and intermediate temperatures.	naphthalene; methyl-naphthalene; biphenyl; ethenylnaphtalene; acenaphtylene; acenaphtene; fluorene; phenanthrene; anthracene
Class 5	*Heavy polyaromatic hydrocarbons (4-5 rings PAH's):* These components condense at relatively high temperature at low concentrations.	fluoranthene; pyrene; benzo-anthracene; chrysene; benzo-fluoranthene; benzo-pyrene; perylene; indeno-pyrene; dibenzo-anthracene; benzo-perylene

Simplified tars can be distinguished in heavy tars and light tars. Heavy tars condense out as the gas temperature drops and cause major fouling, efficiency loss and unscheduled plant stops (figure A.1, the two pictures on the left). The tar dew point is a critical factor for heavy tars and related issues.
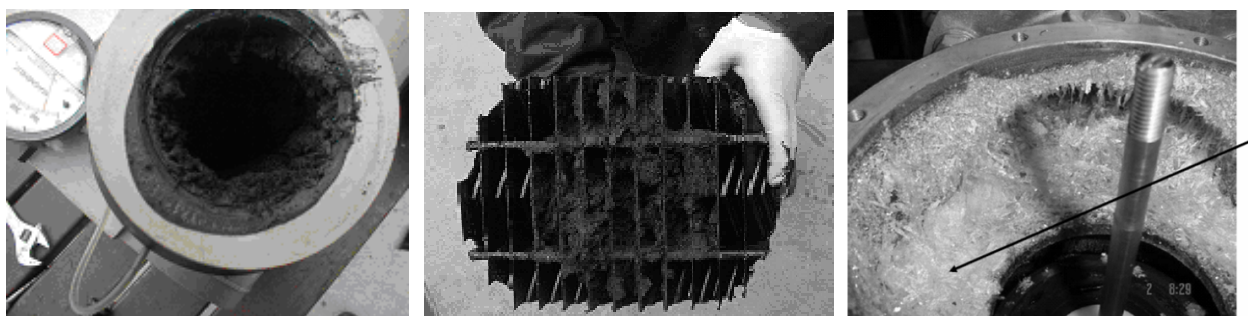
Figure A.1 *Plugging of piping and fouling of equipment with tars*

Light tars like phenol or naphthalene have limited influence on the tar dew point, but are not less problematic. Light tars like phenol chemically pollute the bleed water of downstream condensers and aqueous scrubbers. Naphthalene is important as it is known to crystallise at the inlet of gas engines (figure A.1, the picture on the right) causing a high service demand.

A.2   The tar dewpoint

The lowest temperature in the process is determined by downstream equipment and the application of the producer gas. As typical tar dew points are between 150 °C and 350 °C, and the lowest process temperature is typically 30 °C (compressed gas is even more critical), massive tar condensation and tar problems are inevitable. It is important to realize that the actual tar concentration is not the most important parameter. It is the tar dew point which defines the point at which tars start to be problematic.

The tar dewpoint is the temperature at which the real total partial pressure of tar equals the saturation pressure of tar. Once the actual process temperature becomes lower than the thermodynamic tar dewpoint, tar can condense out. The gas is called over-saturated, although it does not mean that condensation will always happen, as kinetics might be slow. In figure A.2, the relation between the tar dewpoint and the concentration of the different tar classes is presented.
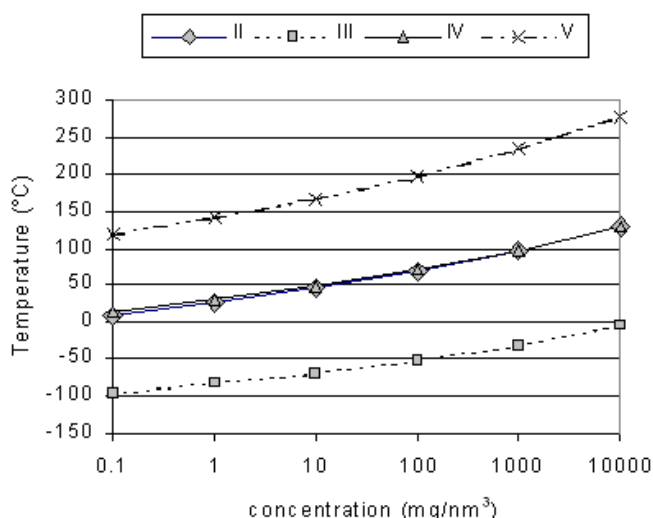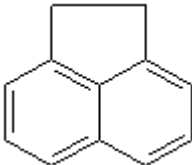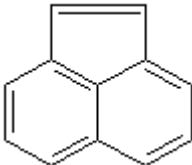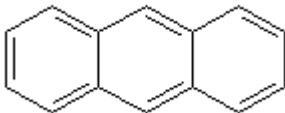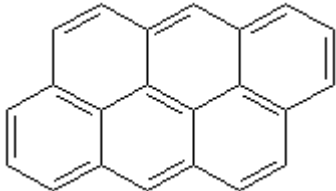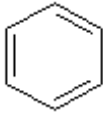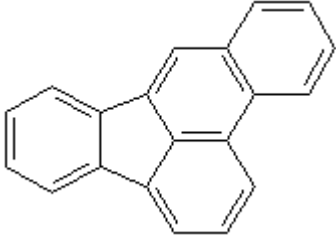
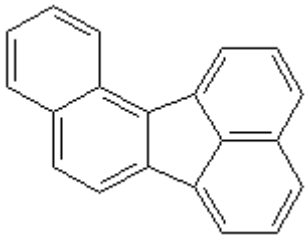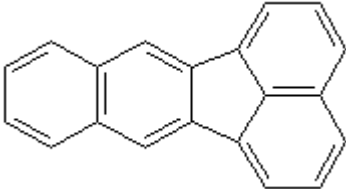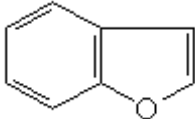Figure A.2 *Relation between the tar dewpoint and the concentration of the different tar classes*
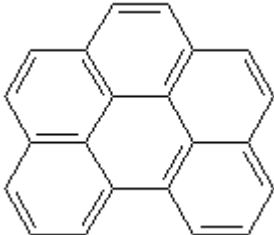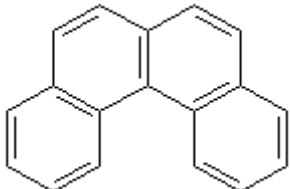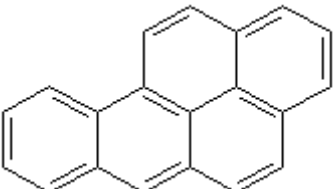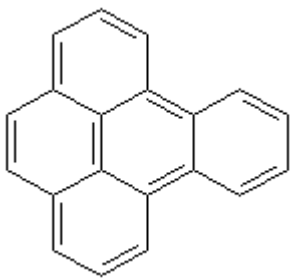
ECN developed a dewpoint model for the calculation of a tar dewpoint from a measured tar composition. The model includes vapour/liquid equilibrium data for the tar compounds in the producer gas from a downdraft or fluidized bed gasifier. The calculation is based on ideal gas behaviour. Raoult's law is applied for the calculation of a mixture of hydrocarbons, using the vapour pressure data of individual compounds. The model has been validated at atmospheric pressure with real producer gas from our laboratory scale BFB gasifier (WOB). The model could predict the tar dewpoint with an accuracy of ±2 °C in the temperature range of 100-175°C. In on going research the model will be validated in the temperature range of 20-100°C.
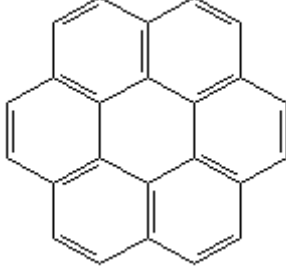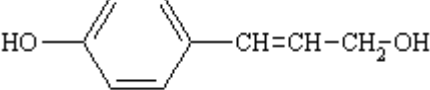
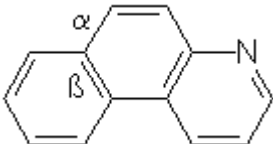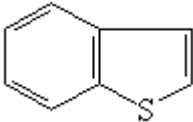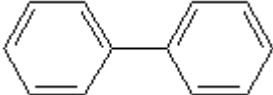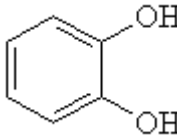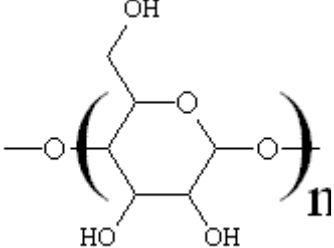More information on the definition of tars, the related issues to tars and the tar dewpoint can be found on the Dahlman OLGA technology website www.olgatechnology.com and the ECN tar dewpoint website www.thersites.nl. On the latter website, an online version of the dewpoint model is made available.
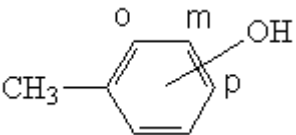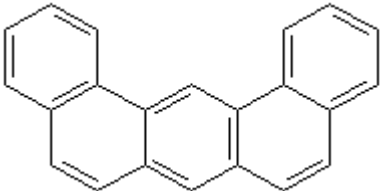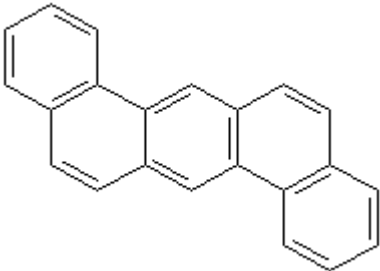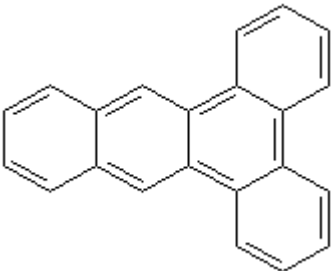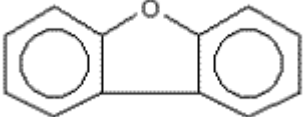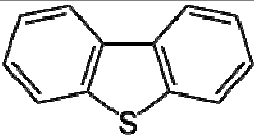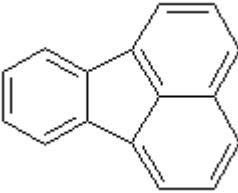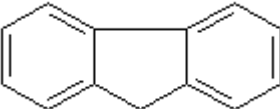
Appendix B   Names and structures of tar compounds
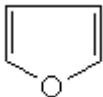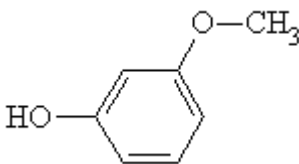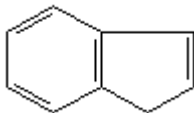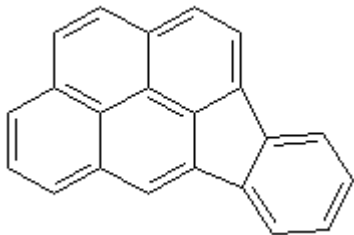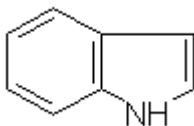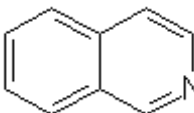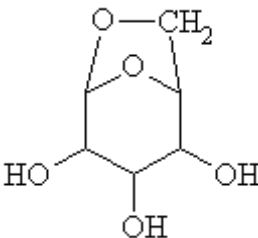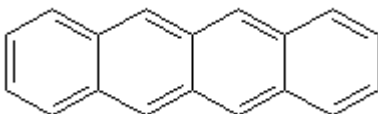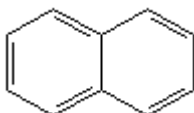
Table B.1 *Names and structures of tar compounds*

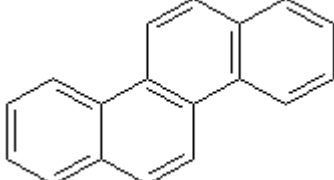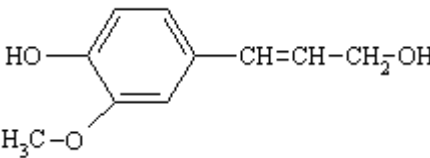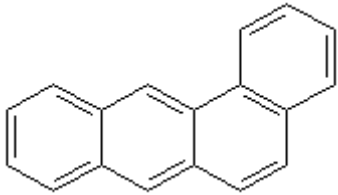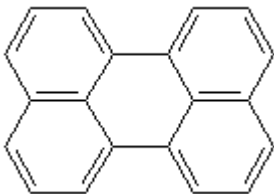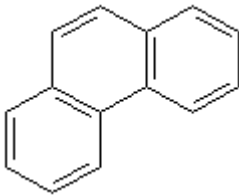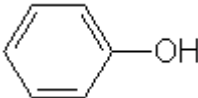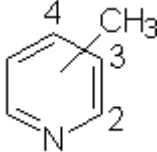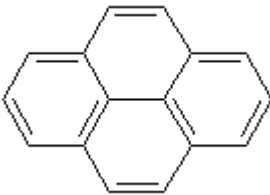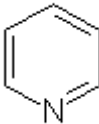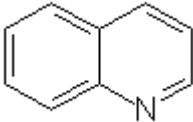| (Trivial) Name	Tar class	Structure	Elementary composition	Molecular weight (g/mol)	Boiling point (°C)
Acenaphtene	4		$C_{12}H_{10}$	154.21	279
Acenaphtylene	4		$C_{12}H_8$	152.19	265-275
Anthracene	4		$C_{14}H_{10}$	178.23	340
Anthanthrene = Dibenzo(def, mno)chrysene = Dibenzo(cd,jk)pyrene	5		$C_{22}H_{12}$	276.33	
Benzene			C_6H_6	78.11	80
Benzo(b)fluoranthene = 3,4-Benzofluoranthene	5		$C_{20}H_{12}$	252.31	

Benzo(j)fluoranthene = 10,11-Benzofluoranthene	5		$C_{20}H_{12}$	252.31	
Benzo(k)fluoranthene = 11,12-Benzofluoranthene	5		$C_{20}H_{12}$	252.31	480
Benzofurane	2		C_8H_6O	118.13	174
Benzo(ghi)perylene	5		$C_{22}H_{12}$	276.33	
Benzo(c)phenanthrene = 3,4-Benzophenanthrene	5		$C_{18}H_{12}$	228.29	
Benzo(a)pyrene = 1,2-Benzopyrene	5		$C_{20}H_{12}$	252.31	310-312
Benzo(e)pyrene = 3,4-Benzopyrene	5		$C_{20}H_{12}$	252.31	310-312
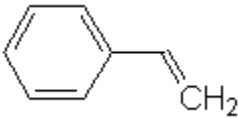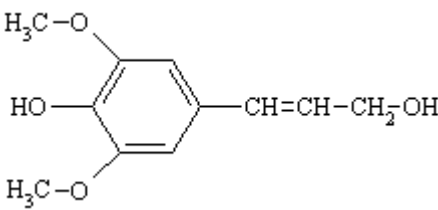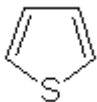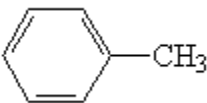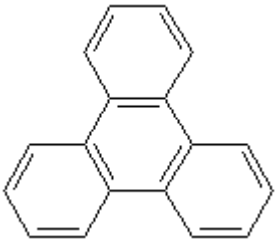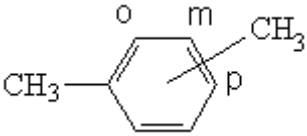
Benzoquinoline	2		$C_{13}H_9N$	179.22	338-350
Benzothiophene	2		C_8H_6S	134.19	221
Biphenyl	4		$C_{12}H_{10}$	154.21	256
Catechol = 1,2-Dihydroxybenzene	2		$C_6H_6O_2$	110.11	245
Cellulose			$(C_6H_{11}O_5)_n$		
Chrysene = 1,2-Benzophenanthrene	5		$C_{18}H_{12}$	228.29	448
Coniferyl alcohol	2		$C_{10}H_{12}O_3$	180.20	163-165
Coronene = Hexabenzobenzene	5		$C_{24}H_{12}$	300.35	525
Coumaryl alcohol	2		$C_9H_{10}O_2$	150.17	

o-Cresol = 2-Hydroxytoluenem-Cresol = 3-Hydroxytoluenep-Cresol = 4-Hydroxytoluene	2		C_7H_8O	108.13	191 202 202
Dibenzo(a,f)anthracene = 1,2:7,8-Dibenzanthracene	5		$C_{22}H_{14}$	278.35	
Dibenzo(a,h)anthracene = 1,2:5,6 Dibenzanthracene	5		$C_{16}H_{10}$	278.35	
Dibenzo(f,h)anthracene = 1,2:3,4 Dibenzanthracene	5		$C_{22}H_{14}$	278.35	
Dibenzofurane	2		$C_{12}H_8O$	168.19	285-287
Dibenzothiophene	2		$C_{12}H_8S$	184.26	332.5
Fluoranthene = 1,2 Benzacenaphtene	4		$C_{16}H_{10}$	202.25	375
Fluorene	4		$C_{13}H_{10}$	166.22	293-295

Name		Structure	Formula	MW	BP
Furane	2		C_4H_4O	68.07	31
Guiaicol = Catechol monomethyl ether = 3-Methoxyphenol	2		$C_7H_8O_2$	124.13	206
Indene	4		C_9H_8	116.16	183
Indeno(1,2,3-cd)pyrene	5		$C_{22}H_{12}$	276.33	
Indole	2		C_8H_7N	117.15	254
Isokinoline = Isoquinoline	2		C_9H_7N	129.16	242
Levoglucosan	2		$C_6H_{10}O_5$	162.14	
Naphtacene = 2,3 Benzanthracene	5		C_9H_8	228.29	sub
Naphthalene	4		$C_{10}H_8$	128.17	218

Naphtanthracene = 1,2 Benzanthracene	5		$C_{18}H_{12}$	228.29	435 (sub)
Perylene = Per-dinaphthalene	4		$C_{20}H_{12}$	252.31	
Phenanthrene	4		$C_{14}H_{10}$	178.23	340
Phenol	2		C_6H_6O	94.11	182
a-Picoline = 2-Methylpyridineb-Picoline = 3-Methylpyridineg-Picoline = 4-Methylpyridine	2		C_6H_7N	93.12	129 144 145
Pyrene = Benzo(d,e,f)phenanthrene	5		$C_{16}H_{10}$	202.25	393
Pyridine	2		C_5H_5N	79.10	116
Pyrrole	2		C_4H_5N	67.09	130-131
Quinoline = Benzo(b)pyridine	2		C_9H_7N	129.16	238

Styrene	3		C_8H_8	104.15	145
Sinapyl alcohol = Syringenin	2		$C_{11}H14_{O4}$	210.22	
Thiophene	2		C_4H_4S	84.13	84
Toluene	3		C_7H_8	92.14	111
Triphenyleen = 9,10 Benzophenanthreen	5		$C_{18}H_{12}$	228.29	425
o-Xylene = 1,2 Dimethylbenzenem-Xylene = 1,3 Dimethylbenzenep-Xylene = 1,4 Dimethylbenzene	2		C_8H_{10}	106.16	144 139 138

Appendix C   Who is who

In this appendix a list of companies or RD&D institutes working on gas cleaning technologies is provided. This is considered to be relevant as in the status report itself it is difficult to refer to all players active in the field of gas cleaning. As such, the main report focused on describing the different technologies and the development status, while in this appendix an alphabetically ordered overview is given of the companies active in the field of gas cleaning with the technology worked on (§C.1) and the specific technologies being developed or patented by different companies (§C.2). The section of the status report in which the specific technology (hence not the company) is discussed as well as the status of the technology development at the end of 2008, is mentioned as well. For the status of the technology development, the following indices are used:

●●	=	commercially available
●	=	commercially available, though not (yet demonstrated) for biomass related thermochemical technologies
○○	=	demonstration phase (pilot or larger)
○	=	demonstration phase, though not for biomass related thermochemical technologies
□□	=	lab-scale testing phase
□	=	lab-scale testing phase, though not for biomass related thermochemical technologies
?	=	current status unknown or unsure

The author of the status report at hand is aware of the fact that this "who is who" list will never be complete. Companies who find their technology development missing may therefore send a brief e-mail with information on their company, the technology developed and some information on this technology. If an update of this "who is who" is considered to be necessary in time, the author will adjust the digital version of this report and will make it available via the publications website of the Energy research Centre of the Netherlands (www.ecn.nl/publications).

C.1   Companies working on…

Company	Technology aimed at removal of …	Detailed information	Status 2008	Status report
Andritz	Tars (cracking/reforming)	Catalytic cracking and reforming (see VTT)	○○	§2.1
BTG	Tars (cracking/reforming)	Reverse-flow catalytic tar converter RF$^®$TC	○○ / ?	§2.1
Cutec	Tars (cracking/reforming)	Catalytic cracking (downstream pilot gasifier)	○○ / ?	§2.1
Ebara Corp	Tars (cracking/reforming)	Catalytic reforming	?	§2.1
ECN	Tars (cracking/reforming)	Plasma cracking (via the GlidArc process)	□□ / ?	§2.1
ECN	Tars (cracking/reforming)	Catalytic cracking (via the TREC process)	□□ / ?	§2.1
Enviropower	Tars (cracking/reforming)	Catalytic cracking	?	§2.1
Europlasma	Tars (cracking/reforming)	Plasma cracking	?	§2.1
FZK	Tars (cracking/reforming)	Partial oxidation	○○	§2.1
FZK	Tars (cracking/reforming)	Catalytic cracking (with char)	○○ / ?	§2.1
IFP	Tars (cracking/reforming)	Catalytic cracking and reforming	?	§2.1
Krupp Koppers	Tars (cracking/reforming)	Partial oxidation	?	§2.1
Madison	Tars (cracking/reforming)	Catalytic filters	□□ / ?	§2.1
Neste Oil	Tars (cracking/reforming)	Catalytic cracking and reforming (see VTT)	○○	§2.1
Nexterra	Tars (cracking/reforming)	Partial oxidation	○○	§2.1
Plasco	Tars (cracking/reforming)	Plasma cracking	●●	§2.1
Stora Enso	Tars (cracking/reforming)	Catalytic cracking and reforming (see VTT)	○○	§2.1
Technical University of Delft	Tars (cracking/reforming)	Catalytic cracking and reforming	□□	§2.1
Technical University of Eindhoven	Tars (cracking/reforming)	Partial oxidation	□	§2.1

Company	Technology aimed at removal of …	Detailed information	Status 2008	Status report
Technical University of Eindhoven	Tars (cracking/reforming)	Plasma cracking	□	§2.1
TPS	Tars (cracking/reforming)	Thermal as well as catalytic tar cracking	○○ / ?	§2.1
Twente University	Tars (cracking/reforming)	Catalytic cracking (with char)	□□ / ?	§2.1
Umsicht	Tars (cracking/reforming)	Catalytic cracking (downstream pilot gasifier)	○○ / ?	§2.1
UPM Kymene	Tars (cracking/reforming)	Catalytic cracking and reforming (see VTT)	○○	§2.1
Valtion Teknillinen	Tars (cracking/reforming)	Catalytic cracking	?	§2.1
VTT	Tars (cracking/reforming)	Catalytic cracking and reforming	○○	§2.1
Babcock & Wilcox Vølund	Tars (physical removal)	Water based scrubbing incl. TARWATC	●●	§2.2
Beth	Tars (physical removal)	Wet ESP filter	●●	§2.2
BTG	Tars (physical removal)	Rotating particle separation	○○ / ?	§2.2
CTU	Tars (physical removal)	RME based scrubbing technology (see TUV)	●●	§2.2
Dahlman	Tars (physical removal)	Oil based scrubbing OLGA	●●	§2.2
ECN	Tars (physical removal)	Oil based scrubbing OLGA (see Dahlman)	●●	§2.2
ECN	Tars (physical removal)	Sawdust filter	○○ / ?	§2.2
ECN	Tars (physical removal)	Rotating particle separator	○○ / ?	§2.2
ECN	Tars (physical removal)	Water scrubbing	○○ / ?	§2.2
Energy Process Technologies	Tars (physical removal)	Oil scrubber	?	§2.2
Envitec	Tars (physical removal)	Wet scrubbing technology	?	§2.2
ETH	Tars (physical removal)	Rotating particle separation	○○ / ?	§2.2
HoSt	Tars (physical removal)	Water scrubbing	○○ / ?	§2.2
HoSt	Tars (physical removal)	Sawdust filter	○○ / ?	§2.2
JFE engineering	Tars (physical removal)	Water based scrubbing (see Babcock & Wilcox)	●●	§2.2
Pall	Tars (physical removal)	Catalytic filter	○○	§2.2
Relax Umwelttechnik GmbH	Tars (physical removal)	Water based scrubbing (see Babcock & Wilcox)	●●	§2.2
Repotec	Tars (physical removal)	RME based scrubbing	●●	§2.2
Schumacher	Tars (physical removal)	Catalytic filter	○○ / ?	§2.2
Dahlman	Chlorine	Oil based OLGA scrubbing (in particular dioxins)	●●	§3.1
ECN	Chlorine	Sodium as well as calcium based adsorption	□□	§3.1
ECN	Chlorine	Oil based OLGA scrubbing (in particular dioxins)	●●	§3.1
FZK	Chlorine	Carbon doped PP based absorption (ADIOX)	○○ / ?	§3.1
Götaverken Miljö	Chlorine	Carbon doped PP based absorption (ADIOX)	○○ / ?	§3.1
Basf	Sulfur	Amine scrubber	●	§3.2
Bayer	Sulfur	Catalytic removal	●	§3.2
Catalysts & Chem Ind Co	Sulfur	Catalytic removal	● / ?	§3.2
Clearwater International Llc	Sulfur	Amine scrubber	● / ?	§3.2
Comprimo	Sulfur	Hydrogenation, absorption and adsorption	● / ?	§3.2
Dorchak Mary Anne	Sulfur	Catalytic removal	?	§3.2
DOW	Sulfur	Amine scrubber	●	§3.2
ECN	Sulfur	Fixed bed HDS as well as ZnO based absorption	□□	§3.2
Elf aquitaine	Sulfur	Regenerative absorption (in particular mercaptans)	?	§3.2
Enviropower Inc	Sulfur	Regenerative absorption	?	§3.2
Envirotherm	Sulfur	Dry and wet desulfurisation	●●	§3.2
Envitec	Sulfur	Amine scrubber	?	§3.2
Gastec NV	Sulfur	Hydrogenation, absorption and absorption	● / ?	§3.2
Haldor Topsøe	Sulfur	Catalytic hydrogenation and absorption	●	§3.2
JGC Corp	Sulfur	Catalytic hydrogenation (in particular COS)	?	§3.2
Johnson Matthey	Sulfur	Catalytic hydrogenation	●	§3.2
Kellogg	Sulfur	Regenerative absorption	?	§3.2
Kema	Sulfur	Catalytic conversion and adsorption	?	§3.2
Krupp Koppers	Sulfur	Amine scrubbing	?	§3.2
Leuna Raffineriegesellschaft	Sulfur	Regenerative adsorption	?	§3.2
Linde	Sulfur	Methanol scrubbing (Rectisol)	●	§3.2
Lurgi	Sulfur	Methanol scrubbing (Rectisol)	●	§3.2
McDermott Technology Inc	Sulfur	Regenerative adsorption	?	§3.2
Mitsubishi Heavy Industries	Sulfur	High-temperature adsorption	□	§3.2
Paques	Sulfur	Biological (THIOPAQ)	●	§3.2
PSI	Sulfur	Fixed bed HDS as well as absorption	○○	§3.2
RCS	Sulfur	Regenerative adsorption	?	§3.2

Company	Technology aimed at removal of …	Detailed information	Status 2008	Status report
RTI	Sulfur	Regenerative adsorption	□	§3.2
Süd Chemie	Sulfur	Catalytic decomposition (in particular COS)	●	§3.2
SulphCatch	Sulfur	Adsorption of organic sulfur compounds	●	§3.2
Teco Energy Inc	Sulfur	Wet scrubbing as well as hydrolysis (in particular COS)	?	§3.2
Texaco	Sulfur	Hydrogenation, absorption and absorption	●	§3.2
Tokyo Gas	Sulfur	Regenerative zeolite ion based desulfurisation	● / ?	§3.2
Uhde	Sulfur	Amine scrubber	●	§3.2
Union Carbide Chem Plastic	Sulfur	Glycol based scrubber	●	§3.2
University of Birmingham	Sulfur	Regenerative absorption	?	§3.2
UOP	Sulfur	Dimethylether & PE-glycol adsorption (Selexol)	●	§3.2
Air Liquide	NH$_3$ and HCN	Water scrubbing	●	§3.3
Basf	NH$_3$ and HCN	Catalytic conversion	●	§3.3
Catalysts & Chem Ind Co	NH$_3$ and HCN	Catalytic conversion	● / ?	§3.3
Dahlman	NH$_3$ and HCN	Water scrubbing	●●	§3.3
ECN	NH$_3$ and HCN	Water scrubbing	□□ / ?	§3.3
Envirotherm	NH$_3$ and HCN	Catalytic reforming	●●	§3.3
Exxon	NH$_3$ and HCN	Catalytic conversion (in particular HCN)	?	§3.3
Exxon	NH$_3$ and HCN	Water scrubbing	?	§3.3
HoSt	NH$_3$ and HCN	Water scrubbing	●●	§3.3
Huels Chemische Werke	NH$_3$ and HCN	Catalytic conversion (in particular HCN)	?	§3.3
JGC Corp	NH$_3$ and HCN	Catalytic conversion	?	§3.3
Krupp Koppers	NH$_3$ and HCN	Amine scrubbing	?	§3.3
Linde	NH$_3$ and HCN	Amine based scrubbing	●	§3.3
Linde	NH$_3$ and HCN	Methanol based scrubbing (Rectisol)	●	§3.3
Lurgi	NH$_3$ and HCN	Methanol based scrubbing (Rectisol)	●	§3.3
Mitsubishi Heavy Industries	NH$_3$ and HCN	Water scrubbing	?	§3.3
Nippon Kokan	NH$_3$ and HCN	Catalytic conversion	?	§3.3
Paques	NH$_3$ and HCN	Biological (ANAMMOX)	●	§3.3
Shell	NH$_3$ and HCN	Water based scrubbing	?	§3.3
Süd Chemie	NH$_3$ and HCN	Catalytic decomposition (in particular HCN)	●	§3.3
Valtion Teknillinen	NH$_3$ and HCN	Catalytic conversion (in particular NH$_3$)	?	§3.3
Air Liquide	Carbon dioxide	Pressure swing based CO$_2$ adsorption	●	§3.4
Basf	Carbon dioxide	Amine scrubber	●	§3.4
Cirmac	Carbon dioxide	Amine based CO$_2$ absorption	●	§3.4
Cirmac	Carbon dioxide	Pressure swing based CO$_2$ adsorption	●	§3.4
Cirmac	Carbon dioxide	Membrane based CO$_2$ separation	●	§3.4
DMT	Carbon dioxide	Amine based CO$_2$ absorption	●	§3.4
GTS	Carbon dioxide	Cryogenic separation of CO$_2$	□	§3.4
Linde	Carbon dioxide	Amine based CO$_2$ absorption	●	§3.4
Linde	Carbon dioxide	Methanol based scrubbing (Rectisol)	●	§3.4
Lurgi	Carbon dioxide	Methanol based scrubbing (Rectisol)	●	§3.4
Process Systems Int	Carbon dioxide	Cryogenic as well as membrane separation of CO$_2$	?	§3.4
Purac	Carbon dioxide	Amine based CO$_2$ absorption	●	§3.4
RWE	Carbon dioxide	Pressure swing based CO$_2$ adsorption	?	§3.4
TNO	Carbon dioxide	Regenerative CO$_2$ absorption	?	§3.4
Uhde	Carbon dioxide	Amine scrubber	●	§3.4
Union Carbide Chem Plastic	Carbon dioxide	Glycol based scrubber	●	§3.4
University of California	Carbon dioxide	Selective separation using CO$_2$ hydrate promoters	?	§3.4
UOP	Carbon dioxide	Dimethylether & PE-glycol adsorption (Selexol)	●	§3.4
ECN	Unsaturated hydrocarbons	Hydrogenation and reforming	□□	§3.5
Engelhard	Unsaturated hydrocarbons	Water based scrubbing	?	§3.5
Haldor Topsøe	Unsaturated hydrocarbons	Hydrogenation and reforming catalyst	●	§3.5
Johnson Matthey	Unsaturated hydrocarbons	Hydrogenation and reforming catalyst	●	§3.5
Linde	Unsaturated hydrocarbons	Methanol based scrubbing (Rectisol)	●	§3.5
Lurgi	Unsaturated hydrocarbons	Methanol based scrubbing (Rectisol)	●	§3.5
PSI	Unsaturated hydrocarbons	Scrubbing, hydrogenation and reforming	○○	§3.5
Süd Chemie	Unsaturated hydrocarbons	Hydrogenation and reforming catalyst	●	§3.5
Alhström	Particles and alkalis	Hot gas filters	●●	§3.6

Company	Technology aimed at removal of …	Detailed information	Status 2008	Status report
Alstom Power	Particles and alkalis	ESP filters	●●	§3.6
Babcock & Wilcox Vølund	Particles and alkalis	ESP filters as well as water based scrubbers	●●	§3.6
BETH	Particles and alkalis	ESP filters	●●	§3.6
Dahlman	Particles and alkalis	Hot gas filters	● / □□	§3.6
Destec Energy Inc	Particles and alkalis	Filters	?	§3.6
DMT	Particles and alkalis	ESP filter	?	§3.6
ECN	Particles and alkalis	Hot gas filters	□□ / ○○ / ?	§3.6
ECN	Particles and alkalis	ESP filter (part of OLGA)	○○	§3.6
ECN	Particles and alkalis	Rotating particle separator	○○ / ?	§3.6
ECN	Particles and alkalis	Cyclones	○○	§3.6
Energy Process Technologies	Particles and alkalis	Oil scrubber	?	§3.6
Envitec	Particles and alkalis	ESP filters and venturi scrubbers	?	§3.6
EWK	Particles and alkalis	ESP filters (in particular for oil)	□□ / ?	§3.6
Foster Wheeler	Particles and alkalis	Hot gas filter	●●	§3.6
HoSt	Particles and alkalis	Cyclones	○○	§3.6
HoSt	Particles and alkalis	Barrier filters	○○	§3.6
IFP	Particles and alkalis	Cyclones	?	§3.6
McGill Air Clean	Particles and alkalis	ESP filters	●●	§3.6
Michaelis	Particles and alkalis	ESP filters (in particular for oil and tar mist)	●	§3.6
MikroPul GmbH	Particles and alkalis	ESP filters (in particular for oil and tar mist)	●	§3.6
Norsk Hydro	Particles and alkalis	Water based scrubber including water filtration	?	§3.6
Pall	Particles and alkalis	Hot gas filter	●●	§3.6
PPC	Particles and alkalis	ESP filters	●●	§3.6
Schumacher	Particles and alkalis	Hot gas filter	●●	§3.6
Shell	Particles and alkalis	Sulfide based gas polishing	?	§3.6
Siemens Westinghouse	Particles and alkalis	Membrane as well as ESP filters for sticky dust	●●	§3.6
Superior Micropowders	Particles and alkalis	Demisters	?	§3.6
Texaco	Particles and alkalis	Water based scrubber (via quench)	?	§3.6
Tri-Mer	Particles and alkalis	Cloud chamber scrubber	●	§3.6
TurboSonic	Particles and alkalis	ESP filters	●	§3.6
Westinghouse	Particles and alkalis	High-temperature adsorption and ceramic filtering	?	§3.6

C.2 Technologies developed by…

Company	Technology aimed at removal of …	Detailed information	Status 2008	Status report
Air Liquide	NH_3 and HCN	Water scrubbing	●	§3.3
Air Liquide	Carbon dioxide	Pressure swing based CO_2 adsorption	●	§3.4
Alhström	Particles and alkalis	Hot gas filters	●●	§3.6
Alstom Power	Particles and alkalis	ESP filters	●●	§3.6
Andritz	Tars (cracking/reforming)	Catalytic cracking and reforming (see VTT)	○○	§2.1
Babcock & Wilcox Vølund	Tars (physical removal)	Water based scrubbing incl. TARWATC	●●	§2.2
Babcock & Wilcox Vølund	Particles and alkalis	ESP filters as well as water based scrubbers	●●	§3.6
Basf	Sulfur	Amine scrubber	●	§3.2
Basf	NH_3 and HCN	Catalytic conversion	●	§3.3
Basf	Carbon dioxide	Amine scrubber	●	§3.4
Bayer	Sulfur	Catalytic removal	●	§3.2
Beth	Tars (physical removal)	Wet ESP filter	●●	§2.2
BETH	Particles and alkalis	ESP filters	●●	§3.6
BTG	Tars (cracking/reforming)	Reverse-flow catalytic tar converter RF®TC	○○ / ?	§2.1
BTG	Tars (physical removal)	Rotating particle separation	○○ / ?	§2.2
Catalysts & Chem Ind Co	Sulfur	Catalytic removal	● / ?	§3.2
Catalysts & Chem Ind Co	NH_3 and HCN	Catalytic conversion	● / ?	§3.3
Cirmac	Carbon dioxide	Amine based CO_2 absorption	●	§3.4
Cirmac	Carbon dioxide	Pressure swing based CO_2 adsorption	●	§3.4
Cirmac	Carbon dioxide	Membrane based CO_2 separation	●	§3.4
Clearwater International Llc	Sulfur	Amine scrubber	● / ?	§3.2
Comprimo	Sulfur	Hydrogenation, absorption and adsorption	● / ?	§3.2

Company	Technology aimed at removal of …	Detailed information	Status 2008	Status report
CTU	Tars (physical removal)	RME based scrubbing technology (see TUV)	●●	§2.2
Cutec	Tars (cracking/reforming)	Catalytic cracking (downstream pilot gasifier)	○○ / ?	§2.1
Dahlman	Tars (physical removal)	Oil based scrubbing OLGA	●●	§2.2
Dahlman	Chlorine	Oil based OLGA scrubbing (in particular dioxins)	●●	§3.1
Dahlman	NH$_3$ and HCN	Water scrubbing	●●	§3.3
Dahlman	Particles and alkalis	Hot gas filters	● / □□	§3.6
Destec Energy Inc	Particles and alkalis	Filters	?	§3.6
DMT	Carbon dioxide	Amine based CO$_2$ absorption	●	§3.4
DMT	Particles and alkalis	ESP filter	?	§3.6
Dorchak Mary Anne	Sulfur	Catalytic removal	?	§3.2
DOW	Sulfur	Amine scrubber	●	§3.2
Ebara Corp	Tars (cracking/reforming)	Catalytic reforming	?	§2.1
ECN	Tars (cracking/reforming)	Plasma cracking (via the GlidArc process)	□□ / ?	§2.1
ECN	Tars (cracking/reforming)	Catalytic cracking (via the TREC process)	□□ / ?	§2.1
ECN	Tars (physical removal)	Oil based scrubbing OLGA (see Dahlman)	●●	§2.2
ECN	Tars (physical removal)	Sawdust filter	○○ / ?	§2.2
ECN	Tars (physical removal)	Rotating particle separator	○○ / ?	§2.2
ECN	Tars (physical removal)	Water scrubbing	○○ / ?	§2.2
ECN	Chlorine	Sodium as well as calcium based adsorption	□□	§3.1
ECN	Chlorine	Oil based OLGA scrubbing (in particular dioxins)	●●	§3.1
ECN	Sulfur	Fixed bed HDS as well as ZnO based absorption	□□	§3.2
ECN	NH$_3$ and HCN	Water scrubbing	□□ / ?	§3.3
ECN	Unsaturated hydrocarbons	Hydrogenation and reforming	□□	§3.5
ECN	Particles and alkalis	Hot gas filters	□□ / ○○ / ?	§3.6
ECN	Particles and alkalis	ESP filter (part of OLGA)	○○	§3.6
ECN	Particles and alkalis	Rotating particle separator	○○ / ?	§3.6
ECN	Particles and alkalis	Cyclones	○○	§3.6
Elf aquitaine	Sulfur	Regenerative absorption (in particular mercaptans)	?	§3.2
Energy Process Technologies	Tars (physical removal)	Oil scrubber	?	§2.2
Energy Process Technologies	Particles and alkalis	Oil scrubber	?	§3.6
Engelhard	Unsaturated hydrocarbons	Water based scrubbing	?	§3.5
Enviropower	Tars (cracking/reforming)	Catalytic cracking	?	§2.1
Enviropower Inc	Sulfur	Regenerative absorption	?	§3.2
Envirotherm	Sulfur	Dry and wet desulfurisation	●●	§3.2
Envirotherm	NH$_3$ and HCN	Catalytic reforming	●●	§3.3
Envitec	Tars (physical removal)	Wet scrubbing technology	?	§2.2
Envitec	Sulfur	Amine scrubber	?	§3.2
Envitec	Particles and alkalis	ESP filters and venturi scrubbers	?	§3.6
ETH	Tars (physical removal)	Rotating particle separation	○○ / ?	§2.2
Europlasma	Tars (cracking/reforming)	Plasma cracking	?	§2.1
EWK	Particles and alkalis	ESP filters (in particular for oil)	□□ / ?	§3.6
Exxon	NH$_3$ and HCN	Catalytic conversion (in particular HCN)	?	§3.3
Exxon	NH$_3$ and HCN	Water scrubbing	?	§3.3
Foster Wheeler	Particles and alkalis	Hot gas filter	●●	§3.6
FZK	Tars (cracking/reforming)	Partial oxidation	○○	§2.1
FZK	Tars (cracking/reforming)	Catalytic cracking (with char)	○○ / ?	§2.1
FZK	Chlorine	Carbon doped PP based absorption (ADIOX)	○○ / ?	§3.1
Gastec NV	Sulfur	Hydrogenation, absorption and absorption	● / ?	§3.2
Götaverken Miljö	Chlorine	Carbon doped PP based absorption (ADIOX)	○○ / ?	§3.1
GTS	Carbon dioxide	Cryogenic separation of CO$_2$	●	§3.4
Haldor Topsøe	Sulfur	Catalytic hydrogenation and absorption	●	§3.2
Haldor Topsøe	Unsaturated hydrocarbons	Hydrogenation and reforming catalyst	●	§3.5
HoSt	Tars (physical removal)	Water scrubbing	○○ / ?	§2.2
HoSt	Tars (physical removal)	Sawdust filter	○○ / ?	§2.2
HoSt	NH$_3$ and HCN	Water scrubbing	●●	§3.3
HoSt	Particles and alkalis	Cyclones	○○	§3.6
HoSt	Particles and alkalis	Barrier filters	○○	§3.6
Huels Chemische Werke	NH$_3$ and HCN	Catalytic conversion (in particular HCN)	?	§3.3

Company	Technology aimed at removal of …	Detailed information	Status 2008	Status report
IFP	Tars (cracking/reforming)	Catalytic cracking and reforming	?	§2.1
IFP	Particles and alkalis	Cyclones	?	§3.6
JFE engineering	Tars (physical removal)	Water based scrubbing (see Babcock & Wilcox)	●●	§2.2
JGC Corp	Sulfur	Catalytic hydrogenation (in particular COS)	?	§3.2
JGC Corp	NH_3 and HCN	Catalytic conversion	?	§3.3
Johnson Matthey	Sulfur	Catalytic hydrogenation	●	§3.2
Johnson Matthey	Unsaturated hydrocarbons	Hydrogenation and reforming catalyst	●	§3.5
Kellogg	Sulfur	Regenerative absorption	?	§3.2
Kema	Sulfur	Catalytic conversion and adsorption	?	§3.2
Krupp Koppers	Tars (cracking/reforming)	Partial oxidation	?	§2.1
Krupp Koppers	Sulfur	Amine scrubbing	?	§3.2
Krupp Koppers	NH_3 and HCN	Amine scrubbing	?	§3.3
Leuna Raffineriegesellschaft	Sulfur	Regenerative adsorption	?	§3.2
Linde	Sulfur	Methanol scrubbing (Rectisol)	●	§3.2
Linde	NH_3 and HCN	Amine based scrubbing	●	§3.3
Linde	NH_3 and HCN	Methanol based scrubbing (Rectisol)	●	§3.3
Linde	Carbon dioxide	Amine based CO_2 absorption	●	§3.4
Linde	Carbon dioxide	Methanol based scrubbing (Rectisol)	●	§3.4
Linde	Unsaturated hydrocarbons	Methanol based scrubbing (Rectisol)	●	§3.5
Lurgi	Sulfur	Methanol scrubbing (Rectisol)	●	§3.2
Lurgi	NH_3 and HCN	Methanol based scrubbing (Rectisol)	●	§3.3
Lurgi	Carbon dioxide	Methanol based scrubbing (Rectisol)	●	§3.4
Lurgi	Unsaturated hydrocarbons	Methanol based scrubbing (Rectisol)	●	§3.5
Madison	Tars (cracking/reforming)	Catalytic filters	□□ / ?	§2.1
McDermott Technology Inc	Sulfur	Regenerative adsorption	?	§3.2
McGill Air Clean	Particles and alkalis	ESP filters	●●	§3.6
Michaelis	Particles and alkalis	ESP filters (in particular for oil and tar mist)	●	§3.6
MikroPul GmbH	Particles and alkalis	ESP filters (in particular for oil and tar mist)	●	§3.6
Mitsubishi Heavy Industries	Sulfur	High-temperature adsorption	□	§3.2
Mitsubishi Heavy Industries	NH_3 and HCN	Water scrubbing	?	§3.3
Neste Oil	Tars (cracking/reforming)	Catalytic cracking and reforming (see VTT)	○○	§2.1
Nexterra	Tars (cracking/reforming)	Partial oxidation	○○	§2.1
Nippon Kokan	NH_3 and HCN	Catalytic conversion	?	§3.3
Norsk Hydro	Particles and alkalis	Water based scrubber including water filtration	?	§3.6
Pall	Tars (physical removal)	Catalytic filter	○○	§2.2
Pall	Particles and alkalis	Hot gas filter	●●	§3.6
Paques	Sulfur	Biological (THIOPAQ)	●	§3.2
Paques	NH_3 and HCN	Biological (ANAMMOX)	●	§3.3
Plasco	Tars (cracking/reforming)	Plasma cracking	●●	§2.1
PPC	Particles and alkalis	ESP filters	●●	§3.6
Process Systems Int	Carbon dioxide	Cryogenic as well as membrane separation of CO_2	?	§3.4
PSI	Sulfur	Fixed bed HDS as well as absorption	○○	§3.2
PSI	Unsaturated hydrocarbons	Scrubbing, hydrogenation and reforming	○○	§3.5
Purac	Carbon dioxide	Amine based CO_2 absorption	●	§3.4
RCS	Sulfur	Regenerative adsorption	?	§3.2
Relax Umwelttechnik GmbH	Tars (physical removal)	Water based scrubbing (see Babcock & Wilcox)	●●	§2.2
Repotec	Tars (physical removal)	RME based scrubbing	●●	§2.2
RTI	Sulfur	Regenerative adsorption	□	§3.2
RWE	Carbon dioxide	Pressure swing based CO_2 adsorption	?	§3.4
Schumacher	Tars (physical removal)	Catalytic filter	○○ / ?	§2.2
Schumacher	Particles and alkalis	Hot gas filter	●●	§3.6
Shell	NH_3 and HCN	Water based scrubbing	?	§3.3
Shell	Particles and alkalis	Sulfide based gas polishing	?	§3.6
Siemens Westinghouse	Particles and alkalis	Membrane as well as ESP filters for sticky dust	●●	§3.6
Stora Enso	Tars (cracking/reforming)	Catalytic cracking and reforming (see VTT)	○○	§2.1
Süd Chemie	Sulfur	Catalytic decomposition (in particular COS)	●	§3.2
Süd Chemie	NH_3 and HCN	Catalytic decomposition (in particular HCN)	●	§3.3
Süd Chemie	Unsaturated hydrocarbons	Hydrogenation and reforming catalyst	●	§3.5

Company	Technology aimed at removal of …	Detailed information	Status 2008	Status report
SulphCatch	Sulfur	Adsorption of organic sulfur compounds	●	§3.2
Superior Micropowders	Particles and alkalis	Demisters	?	§3.6
Technical University of Delft	Tars (cracking/reforming)	Catalytic cracking and reforming	□□	§2.1
Technical University of Eindhoven	Tars (cracking/reforming)	Partial oxidation	□	§2.1
Technical University of Eindhoven	Tars (cracking/reforming)	Plasma cracking	□	§2.1
Teco Energy Inc	Sulfur	Wet scrubbing as well as hydrolysis (in particular COS)	?	§3.2
Texaco	Sulfur	Hydrogenation, absorption and absorption	●	§3.2
Texaco	Particles and alkalis	Water based scrubber (via quench)	?	§3.6
TNO	Carbon dioxide	Regenerative CO_2 absorption	?	§3.4
Tokyo Gas	Sulfur	Regenerative zeolite ion based desulfurisation	● / ?	§3.2
TPS	Tars (cracking/reforming)	Thermal as well as catalytic tar cracking	○○ / ?	§2.1
Tri-Mer	Particles and alkalis	Cloud chamber scrubber	●	§3.6
TurboSonic	Particles and alkalis	ESP filters	●	§3.6
Twente University	Tars (cracking/reforming)	Catalytic cracking (with char)	□□ / ?	§2.1
Uhde	Sulfur	Amine scrubber	●	§3.2
Uhde	Carbon dioxide	Amine scrubber	●	§3.4
Umsicht	Tars (cracking/reforming)	Catalytic cracking (downstream pilot gasifier)	○○ / ?	§2.1
Union Carbide Chem Plastic	Sulfur	Glycol based scrubber	●	§3.2
Union Carbide Chem Plastic	Carbon dioxide	Glycol based scrubber	●	§3.4
University of Birmingham	Sulfur	Regenerative absorption	?	§3.2
University of California	Carbon dioxide	Selective separation using CO_2 hydrate promoters	?	§3.4
UOP	Sulfur	Dimethylether & PE-glycol adsorption (Selexol)	●	§3.2
UOP	Carbon dioxide	Dimethylether & PE-glycol adsorption (Selexol)	●	§3.4
UPM Kymene	Tars (cracking/reforming)	Catalytic cracking and reforming (see VTT)	○○	§2.1
Valtion Teknillinen	Tars (cracking/reforming)	Catalytic cracking	?	§2.1
Valtion Teknillinen	NH_3 and HCN	Catalytic conversion (in particular NH_3)	?	§3.3
VTT	Tars (cracking/reforming)	Catalytic cracking and reforming	○○	§2.1
Westinghouse	Particles and alkalis	High-temperature adsorption and ceramic filtering	?	§3.6