Tar reforming through autothermal partial oxidation combined with catalytic ammonia reduction

Tunå, Per; Bauer, Fredric; Hulteberg, Christian

2013

Citation for published version (APA):
Tunå, P., Bauer, F., & Hulteberg, C. (2013). *Tar reforming through autothermal partial oxidation combined with catalytic ammonia reduction*. (SGC Rapport; Vol. 2013:276). Swedish Gas Technology Centre.

Total number of authors:
3

LUND UNIVERSITY

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

SGC Rapport 2013:276

Tar reforming through autothermal partial oxidation combined with catalytic ammonia reduction

(Tjärreformering via autoterm partiell oxidation kombinerad med katalytisk ammoniak reduktion)

Per Tunå, Fredric Bauer, Christian Hulteberg

"Catalyzing energygas development
for sustainable solutions"

SGC Svenskt
Gastekniskt
CenterAB

Svenskt Gastekniskt Center/Swedish Gas Technology Centre
Scheelegatan 3
SE-211 28 MALMÖ
+46 40 6800760
info@sgc.se
www.sgc.se

Denna rapport är tryckt på papperskvaliteten MultiDesign Ivory 240 g/m^2 (pärm) samt 90 g/m^2 (inlaga). Vårt val av papper är mycket medvetet. MultiDesign Ivory är tillverkat av VIDA Paper AB i Lessebo i Småland. Pappersmassan utgörs av svensk granvedsråvara, förvaltad i enlighet med PEFC, som framställts till massa med hjälp av en sur magnesiumbisulfitprocess följd av väterperoxidblekning (TCF). Pappret är fritt från optiska vitmedel (OBA), vilka oftast är fossilbaserade. Inte heller är pappret bestruket med något icke-förnybart mineral. Papprets CIE-vithet är 60. Denna svaga gulton ger bästa möjliga läsbarhet och innebär jämfört med ett kritvitt papper en kostnadseffektivare produktion och en avsevärt lägre miljöpåverkan vid massablekningen.

Tryckt av Lunds kommun, Serviceförvaltningen, Lund 2013
ISSN 1102-7371

TAR REFORMING THROUGH PARTIAL OXIDATION COMBINED WITH CATALYTIC AMMONIA REDUCTION (TJÄRREFORMERING VIA PARTIELL OXIDATION KOMBINERAD MED KATALYTISK AMMONIAK REDUKTION)

Per Tunå, Fredric Bauer, Christian Hulteberg

Denna studie har finansierats av:
Energimyndigheten
ABB Corporate Research
Alufluor AB
DGC
E.ON Gasification Development AB
E.ON Sverige AB
Göteborg Energi AB
Institutionen för Kemiteknik på LTH
Statoil ASA
Stockholm Gas AB
Tekniska Verken i Linköping AB
ÅForsk
Öresundskraft AB

Postadress och Besöksadress
Scheelegatan 3
212 28 MALMÖ

Telefonväxel
040-680 07 60

Telefax
0735-279104

E-post
info@sgc.se

Hemsida
www.sgc.se

Svenskt Gastekniskt Center AB, SGC

SGC är ett spjutspetsföretag inom hållbar utveckling med ett nationellt uppdrag. Vi arbetar under devisen *”Catalyzing energygas development for sustainable solutions”*. Vi samordnar branschgemensam utveckling kring framställning, distribution och användning av energigaser och sprider kunskap om energigaser. Fokus ligger på förnybara gaser från rötning och förgasning. Tillsammans med företag och med Energimyndigheten och dess kollektivforskningsprogram *Energigastekniskt utvecklingsprogram* utvecklar vi nya möjligheter för energigaserna att bidra till ett hållbart samhälle. Tillsammans med våra fokusgrupper inom *Rötning*, *Förgasning och bränslesyntes*, *Distribution och lagring*, *Kraft/Värme* och *Gasformiga drivmedel* identifierar vi frågeställningar av branschgemensamt intresse att genomföra forsknings-, utvecklings och/eller demonstrationsprojekt kring. Som medlem i den europeiska gasforskningsorganisationen GERG fångar SGC också upp internationella perspektiv på utvecklingen inom energigasområdet.

Resultaten från projekt drivna av SGC publiceras i en särskild rapportserie – *SGC Rapport*. Rapporterna kan laddas ned från hemsidan – www.sgc.se. Det är också möjligt att prenumerera på de tryckta rapporterna. SGC svarar för utgivningen av rapporterna medan rapportförfattarna svarar för rapporternas innehåll.

SGC ger också ut faktabroschyrer kring olika aspekter av energigasers framställning, distribution och användning. Broschyrer kan köpas via SGC:s kansli.

SGC har sedan starten 1990 sitt säte i Malmö. Vi ägs av Eon Gas Sverige AB, Energigas Sverige, Swedegas AB, Göteborg Energi AB, Lunds Energikoncernen AB (publ) och Öresundskraft AB.

Malmö 2013

Martin Ragnar
Verkställande direktör

SGC Rapport 2013:276

Swedish Gas Technology Centre, SGC

SGC is a leading-edge company within the field of sustainable development having a national Swedish assignment. We work under the vision of *"Catalyzing energygas development for sustainable solutions"*. We co-ordinate technical development including manufacture, distribution and utilization of energy gases and spread knowledge on energy gases. Focus is on renewable gases from anaerobic digestion and gasification. Together with private companies and the Swedish Energy Agency and its frame program *Development program for energy gas technology* we develop new solutions where the energygases could provide benefits for a sustainable society. Together with our focus groups on *Anaerobic digestion*, *Gasification and fuel synthesis*, *Distribution and storage*, *Power/Heat* and *Gaseous fuels* we identify issues of joint interest for the industry to build common research, development and/or demonstrations projects around. As a member of the European gas research organization GERG SGC provides an international perspective to the development within the energygas sector

Results from the SGC projects are published in a report series – *SGC Rapport*. The reports could be downloaded from our website – www.sgc.se. It is also possible to subscribe to the printed reports. SGC is responsible for the publishing of the reports, whereas the authors of the report are responsible for the content of the reports.

SGC also publishes fact brochures and the results from our research projects in the report series *SGC Rapport*. Brochures could be purchase from the webiste.

SGC is since the start in 1990 located to Malmö. We are owned by Eon Gas Sverige AB, Energigas Sverige, Swedegas AB, Göteborg Energi AB, Lunds Energikoncernen AB (publ) and Öresundskraft AB.

Malmö, Sweden 2013

Martin Ragnar
Chief Executive Officer

Authors' foreword

This project has been developed as a continuation on a part of the Green Syngas project which was financed by the 7th Framework Program of the European Union. The work within this research project has been conducted at the Department of Chemical Engineering at Lund University by doctoral student Per Tunå under supervision by Professor Hans T. Karlsson and PhD Christian Hulteberg at Lund University together with Associate professor Jan Brandin at Linnæus University.

Following persons have constituted the reference group;
Jörgen Held, SGC on consultancy basis (project coordinator)
Esther Ochoa-Fernández, Statoil ASA
Ingemar Gunnarsson, Göteborg Energi AB
Niels Bjarne Rasmusson, DGC

Summary

This research project has aimed to develop, construct and conduct laboratory experiments with a regenerative reverse flow reactor for cracking of tar components in producer gas from a biomass gasifier intended for production of biobased synthetic natural gas (Bio-SNG). When biomass is gasified the main components in the producer gas are carbon monoxide, carbon dioxdide, hydrogen, methane and lower hydrocarbons. A share of the hemicellulose will however not decompose completely in the gasifier, but instead form tar components, hydrocarbons which are heavier than benzene and often consist of one or many C_6-rings. The tar components contain a significant share of the heating value of the gas, which is lost if the components are not converted to SNG-components. Further, the tar components tend to condense, clog and harm downstream equipment operated at lower temperatures, which makes the operation of the bio-SNG process unreliable. It is thus very important to convert the tar components to lower hydrocarbons or syngas components.

Further, the producer gas from a biomass gasifier also contains significant amounts of ammonia, due to the nitrogen content of the biomass feedstock. The ammonia can damage downstream catalysts in a synthesis process and in the case of combustion, it will form NO_x which is corrosive and contributes to air pollution. NO_x emissions are normally abated using selective catalytic reduction (SCR) in which ammonia is added to react with NO_x and convert it to nitrogen. Removing the ammonia from the producer gas can be done by decomposition at higher temperatures or by a reverse SCR, a new process which has been proposed and tested in this project.

A regenerative reverse flow reactor with a bed consisting of dolomite granules was constructed. Initially, it was intended to combine both tar cracking and reverse SCR in this reactor, but that proved to be unfavorable for the process. Reverse flow systems have a very high thermal efficiency as the whole bed acts as a thermal buffer, being heated by an exothermic reaction and cooled by the incoming gas. When reversing the flow the heat stored in the bed is used to support the reaction with a very high efficiency. Apart from being a good thermal buffer, calcined dolomite has been proven to have a catalytic effect on both tar cracking and ammonia decomposition.

Experiments were performed in which the regenerative reverse flow reactor was operated in a lab with a synthetic producer gas and a model tar compound, 1-methylnaphthalene. At temperatures of 700-800°C, a conversion of about 90% of 1-methylnaphthalene (also converted into other tars) and a total tar conversion of about 60% was possible. Ammonia was decomposed to about 50%.

The reverse SCR experiments were performed in another setup using a catalysts based V_2O_5 and H-mordenite at temperatures of 300-400°C and using different stoichiometric correlations between NH_3 and NO_2. The conversion was almost 100% in both cases, but whereas the V_2O_5 performed best in the interval 300-350°C the H-mordenite required temperatures of 370-400°C.

The reverse flow reactor with a dolomite bed seems suitable for tar cracking applications, but has to be tested with more complex tars and real producer gas. That it also decomposes ammonia makes it even more interesting. Reverse SCR for ammonia oxidation does seem promising but must be further investigated.

Sammanfattning på svenska

Förgasning av biomassa ger en gas som förutom vätgas, kolmonoxid, koldioxid och vatten även innehåller en del föroreningar så som tjäror och ammoniak. Beroende på hur förgasningen utförs så finns det även metan i betydande mängder. Om förgasningen och tillhörande nedströmsprocesser har för avsikt att producera syntetisk naturgas, så är det en fördel att behålla så stor del av metanet som bildas vid förgasningen i slutprodukten för att på så vis minska mängden gas som behöver processas. Tjärorna i gasen efter en förgasare kan innehålla ca 10 % av det totala energiinnehållet i gasen. Tyngre tjäror har en relativt hög daggpunkt vilket medför att de kondenserar ut när gasen kyls ner före nedströmsprocesser efter förgasaren. Kondenserande tjäror sätter igen rör och belägger värmeväxlarytor vilket medför sämre värmeöverföring samt kan belägga katalysatorer nedströms vilket kan leda till att den utsatta katalysatorn helt slutar att fungera.

Ammoniak kan, beroende på förgasningsteknik och råvara, finnas i halter från flera hundra vppm upp till några volymsprocent. Ammoniak kan tas bort från gaser med hjälp av skrubbrar men det förstör inte ammoniaken, det flyttar den från gasen till vätskan. Flera tusen ppm ammoniak i gasen medför att skrubbervätskan får höga halter ammoniak. En vätska med höga halter ammoniak behöver renas innan den kan släppas ut vilket medför kostnader. Om gasen från förgasaren bränns direkt, till exempel i en förbränningsmotor, utan rening så bildas höga halter NO_X när ammoniaken oxideras. NO_X är utsläppskontrollerat då det både är korrosivt och försurande.

Det här projektet har fokuserat på rening av två betydande komponenter i produktgasen från förgasare, tjäror och ammoniak. Arbetet har bestått av konstruktionen av en laborativ uppställning för krackning av tjäror och en uppställning för selektiv oxidation av ammoniak. De katalysatorerna som traditionellt används för krackning och reformering av kolväten är ofta baserade på nickel och har hög aktivitet. Problemet med nickel är att det är mycket känsligt för svavel. Svavel finns som H_2S i halter runt 150 ppm och som organiskt bundet svavel i gasen producerat i en träflisförgasare. Halterna varierar beroende på vilken råvara som används. Detta är för mycket för de traditionella nickelbaserade katalysatorerna. Det är därför mycket viktigt att utveckla en process som kan konvertera tjärorna till syntesgas och metan, utan att använda mer energi än traditionella system och som samtidigt är robust och tålig mot föroreningarna som finns i gasen.

Reaktortekniken bygger på en tidigare undersökt teknik som kallas *reverse flow* som går ut på att flödesriktningen på gasen i byter riktning under drift. Detta koncept möjliggör höga verkningsgrader för processen då en mycket effektiv värmeväxling sker mellan utgående och inkommande gas. För att denna effektiva värmeväxling ska ske så krävs ett packningsmaterial i reaktorn som fungerar som värmebuffert. Packningsmaterialet behöver vara finfördelat och ha en tillräckligt liten partikelstorlek för att få så stor yta som möjligt utan att vara för smått, då tryckfallet blir för stort. Dessutom behöver materialet ha en bra värmekapacitet och med fördel låg värmeledningsförmåga. På grund av dessa egenskaper så passar keramiska material bäst då de har en hög värmekapacitet och samtidigt låg värmeledningsförmåga. I det här projektet så har ett keramiskt material, dolomit, valts. Dolomit har, förutom de tidigare fysikaliska egenskaperna, kemisk aktivitet för tjärkrackning. Dolomit som består av $CaCO_3/MgCO_3$ behöver kalcineras före

användning vilket ger CaO/MgO istället för karbonaterna. Det är den kalcinerade dolomiten som är aktiv för tjärkrackning. Kalcinering är en energikrävande process och det skedde inför försöken i rapporten i reaktorn med hjälp av förbränning av metanol/vätgas.

Ammoniaksönderdelningsförsöken bygger på teknik som används för rening av NO_X i rökgaser där NO_X reduceras med ammoniak över en katalysator. Denna process kallas selective catalytic reduction eller SCR. Det som skiljer mellan rökgasrenings SCR och den som tillämpas här är att i vanlig SCR så finns ett överskott på syre närvarande från till exempel en panna. Gasen som produceras i en förgasare innehåller inget syre utan har istället stora kvantiteter vätgas och kolmonoxid. Både vätgas och kolmonoxid har reducerande egenskaper till skillnad från gaser innehållande syre som är oxiderande. Ammoniak SCR utfördes i en separat glasreaktor med två industriella SCR katalysatorer: En vanadin-baserad och en H-mordenit. Ammoniakkrackning är en process som sker samtidigt som kolväteskrackning i samma reaktor och bildar vätgas och kvävgas. Försöken med selektiv oxidation av ammoniak skulle ursprungligen göras i samma reaktor som tjärkrackningen men gjordes i en separat reaktor då det inte ansågs vara möjligt att genomföra med befintlig utrustning samt att det troligtvis inte hade medfört några fördelar. Det hade däremot medfört nackdelar så som fördelning av SCR-katalysator i ett tvärsnitt av tjärkrackern. Ammoniakkrackningsförsöken gjordes i tjärkrackningsreaktorn under rätta betingelser.

Tjärkrackningsreaktorn har fyra rör för syreinjektion i toppen och fyra i botten, för att öka temperaturen och på så sätt tillföra den nödvändiga energin som behövs för att kracka tjärorna. Rören fylls med bäddmaterial när bäddmaterialet fylls på i reaktorn. Ett av problemen med den reaktorn som uppstod var att fördelningen av bäddmaterial inte var symmetrisk i de fyra rören i toppen av reaktorn. Detta resulterar i ett lägre tryckfall i de rören med mindre bäddmaterial vilket medför ett högre flöde av syre. Om flödet av syre inte är lika i alla rören så blir inte fördelning i reaktortvärsnittet efter syreinmatningen symmetriskt. Omsättningen kan därmed variera i tvärsnittet, vilket observerades under uppvärmning av reaktorn då förbränningsprodukterna varierade beroende på flödesriktning. Med en flödesriktning från toppen till botten så fanns vätgas och kolmonoxid i utgående gas vid en stökiometrisk mängd syretillskott. Fullständig förbränning observerades då flödet gick från botten till toppen.

Reaktorn matades med en gas från flaskor med hjälp av massflödesregulatorer med en sammansättning motsvarande den från en förgasare men med enbart en tjärkomponent. 1-metylnaftalen användes som tjärkomponent då den är flytande vid rumstemperatur, vilket underlättar inmatningen avsevärt. Till reaktorn finns ett styrsystem som styr flödesregulatorer och ventiler samt gör insamling av temperaturer och mätning av CO, CO_2, H_2, NH_3 samt CH_4. Analysen av tjärkomponenter görs med manuell utsugning av gas och eluering med lösningsmedel och därefter utförs en GC-analys på lösningen. Försök har gjorts med tre inflöden på 0.5, 0.85 samt 1.2 Nm^3/h och med temperaturer mellan 700 och 800 °C.

Analyserna av gasen som passerat krackern visar på en omsättning runt 90% av 1-metylnaftalen samt runt 60% totalomsättning av tjäror vilket inkluderar bensen, toluen och naftalen. Metanbevarandet i gasen är av intresse och resultaten från experimenten visar till och med en ökning av metanhalten för vissa fall. Detta tyder på att kolet i tjäran som krackas övergår till metan. Förhållandet mellan H_2 och CO även kallat H_2:CO kvoten är av intresse för nedströmsprocesser och bör för till exempel syntetisk naturgas ligga på 3:1. Dolomiten i reaktorn är aktiv för vattengas shift reaktionen och gasen som lämnar reaktorn vid 290 °C är nästan i jämvikt vid de lägre flödena vilket resulterar i H_2:CO kvoter på 5-6:1. Det hade varit av intresse att ha en högre temperatur ut från reaktorn men begränsningar på ventiler gjorde att detta var omöjligt.

När ammoniak körs in i reaktorn tillsammans med övrig gas så visar resultaten på en omsättning av ammoniak på ca 50% över tjärkrackningskatalysatorn. Ammoniakomsättningen i SCR-reaktorn visar på en omsättning på nästan 100% för båda SCR katalysatorerna. Det behövs dock vidare studier på verklig gas från en förgasare för att fastställa livslängder för katalysatorerna i den reducerande miljön samt med de föroreningar som finns i gasen.

Tjärkrackern som har konstruerats med dolomit som bäddmaterial har en hög omsättning av tjäror och att den dessutom har en hög omsättning av ammoniak gör den mycket intressant för fortsatt forskning. Det som behövs för att verkligen fastställa möjligheterna är att köra reaktorn med verklig gas från en förgasare. Verklig gas innehåller fler tjärkomponenter och andra föroreningar som är svåra att efterskapa på labb. Det är först efter en omfattande utredning med verklig gas som det går att fastställa prestandan på tjärkrackern med den gasen som den ska användas med.

Innehåll

1 Introduction

1.1 Background

The interest for renewable fuels has increased and will continue to do so steadily, if current energy and climate policy continue to develop as planned. Biodiesel, methyl esters, produced from vegetable oils and animal fats, alcohols produced by fermentation of sugar or starch containing agricultural products, are examples on the first generation of bio-fuels. It is however, controversial to use food for fuel purposes in a world where the demand for food and feed crops are increasing, which has also been reflected in recent policy developments within the European Union, e.g. the goal of reaching 10% renewable fuels within the transport sector is now under consideration as it seems to compete too directly with production of food and feed.

Second generation bio-fuels production is based on utilising non-food crops for the production of fuels, for instance cellulose. Thus agricultural waste, forest residues and energy crops become useful for fuel production (Albertazzi et al., 2005). One important process for the efficient utilisation of cellulose rich biomass is gasification. Gasification is a well proven technique for processing of fossil fuels, like coal, and has been used extensively. During the gasification, the carbon containing material is partly burnt by contact with air or oxygen. Due to the released heat, the presence of oxygen and/or steam, CO, CO_2 and a multitude of chemical and physical reactions and processes that occur converts the solid fuel into a gas and an ash fraction.

The produced gas, the synthesis gas, contains as major components CO, CO_2, H_2, H_2O and N_2 if air is used for the gasification. However, it also contains some lower hydrocarbons (C_1-C_3), tars (C_{6+}) and a multitude of smaller amounts of contaminants such as H_2S and HCN, but also significant amounts of NH3. The actual composition of the gas depends on the type of gasifier, operating conditions and the type and origin of the used fuel, e.g. coal or biomass. A substantial part of the chemically bonded heat in the gas is contained in the tar fraction and the lower hydrocarbons, approximately 50% depending on gasifier type and process conditions (Tunå, Svensson, & Brandin, 2010). It is thus necessary to convert these hydrocarbons and tars into useful compounds to obtain a high efficiency of the process. Further, the tars may also cause problems in downstream processes if not converted to lighter compounds. The common procedure for this process is the steam reforming, SREF.

The hydrocarbons are gasified and mixed with steam and the gas passes through an externally heated reactor (normally multiple fired-tubes) filled with SREF-catalyst that converts the hydrocarbons. A later development is the secondary reformer in conjunction with an ordinary SREF-unit to improve the conversion of methane. This process, the secondary reformer process, can be used as a standalone process, usually with natural gas as fuel, and is then denoted: Auto-Thermal Reforming (ATR). In an ATR-unit an oxidizer, air or oxygen, is injected into the reactor and a part of the fuel is combusted to increase the temperature. The hot gas then passes a catalytic bed and the remaining hydrocarbons are converted into synthesis gas. In a rather similar process, Partial Oxidation (POX), an oxidant is also added and a part of the fuel is burnt in a flame. POX can be operated with and without a catalyst. In non-catalytic POX, the reforming takes place homogenously in the gas phase. Due to the un-catalysed reactions, the gas temperature has to be increased more in POX than in the case of ATR and this decreases the yield of synthesis gas compared to ATR.

1.2 Scope and aims

In the previous work, the focus was to develop a model of a POX reactor and investigate the possibilities to use it for alternating flow to convert methane to syngas components. It was however discovered that the very high temperatures needed for this process made it very difficult to implement this theory in a real reactor system. Using the same type of reactor, this project aims to design a process for the partial oxidation of tars in a gas stream from a biomass gasifier.

Further, as mentioned above, the gas stream from the gasifier contains significant amounts of ammonia, there are reported values of approx. 3,000 vppm from PCFB gasifiers. Although the ammonia is not thermodynamically stable at the conditions in which it appears in this context, the elimination is slow due to kinetic constraints. If the product gas is intended for direct combustion, e.g. in a BIGCC (Biomass Integrated Gasification Combined Cycle), it will be converted into NOx which is not only a severe pollutant but also corrosive to the equipment. If the gas is instead intended for a GTL (gas-to-liquid) fuel process, the ammonia might poison downstream catalysts and cause severe problems for the process. Thus, the removal of ammonia from the gas stream is an important priority. This project aims to integrate a process for the chemical conversion and elimination of ammonia into the reforming process needed for tar conversion, to ensure a high-efficiency process and a clean gas suitable for advanced downstream applications.

As no gasifier is present, a model synthesis gas is used by mixing gas from bottles using mass flow controllers. Only one tar compound, 1-methylnaphtalene, is used instead of the multitude of hydrocarbons usually found in producer gas. This is a limitation of the experiments and future work should be on a real producer gas. The producer gas would also contain other contaminants such as alkalines, sulphur and lower hydrocarbons such as acetylene and ethylene not present in the model gas.

Because the reactor is fabricated from stainless steel, it is impossible to achieve the high temperatures necessary for complete methane reforming – which is also wanted for this project. So although it is based on the previous work done on partial oxidation of methane it is now focused on reforming of hydrocarbons except methane.

1.3 Report disposition

This report presents the work performed to develop the regenerative, alternating flow POX reactor which was developed and modeled earlier. In chapter 2 the theoretical background for tar removal as well as ammonia decomposition and reversed SCR is presented; chapter 3 describes the experimental setup which has been designed and constructed within this project; chapter 4 presents the results from the experiments on both tar removal and ammonia reduction; chapter 5 discusses the implications of the results and the need for further research on the process.

2 Theoretical frame

This chapter presents the theoretical background for the project. First, tar reforming and partial oxidation (POX) is presented, thereafter the theory of regenerative, counterflow reactors and the results from earlier modeling of this reactor type. Finally, methods for reduction of ammonia are presented with a focus on reversed selective catalytic reduction (SCR). This report deals with tars formed during biomass gasification but does not present technologies for the gasification process, interested readers are referred to recent reports by SGC on this subject (Held, 2012).

2.1 Tars – formation and removal

In biomass gasification, the formation of tars is a well-known problem which hinders the utilization of produced gas in a range of applications due to the harm the tars can cause to materials and equipment. Senior researchers within the field have even called gas cleaning and tar removal “the Achilles heel of the [biomass gasification] process” (Rabou, Zwart, Vreugdenhil, & Bos, 2009). Tars are formed during the gasification process as the macro-molecular compunds of ligno-cellulosic biomass is decomposed into smaller fragments. Although there is no universally accepted definition of the word tar in this context, the definition presented in the exhaustive report on the subject by Milne and Evans is often referred (Evans & Milne, 1997). The report suggests a definition of tar which reads *“the organics, produced under thermal or partial-oxidation regimes (gasification) of any organic material, are called “tars” and are generally assumed to be largely aromatic”*. As this report does not delve deeply into the formation and difference between all the tar compounds that can be detected in gas from a full-scale biomass gasifier, but simply uses a model compound for the experiments, this definition is useful.

2.1.1 Tar characterization and formation

As no universal definition of the concept of tars exists, characterization and lumping of tar compounds is also performed according to different standards. Tar compounds may be characterized as primary, secondary or tertiary tars (Milne, Abatzoglou, & Evans, 1998). Compounds of the primary type are products derived directly from cellulose, hemi-cellulose or lignin with a high oxygen content, secondary tars consist of phenolics and olefins, whereas tertiary tars can be either condensed tertiary, i.e. poly-aromatics without substituent groups, or alkyl tertiary such as methyl derivatives of poly-aromatics. The reaction scheme presented in Figure 1 shows how primary tars are formed initially from the biomass constituents, thereafter are converted into secondary tars which can associate to the more complex tertiary tars.

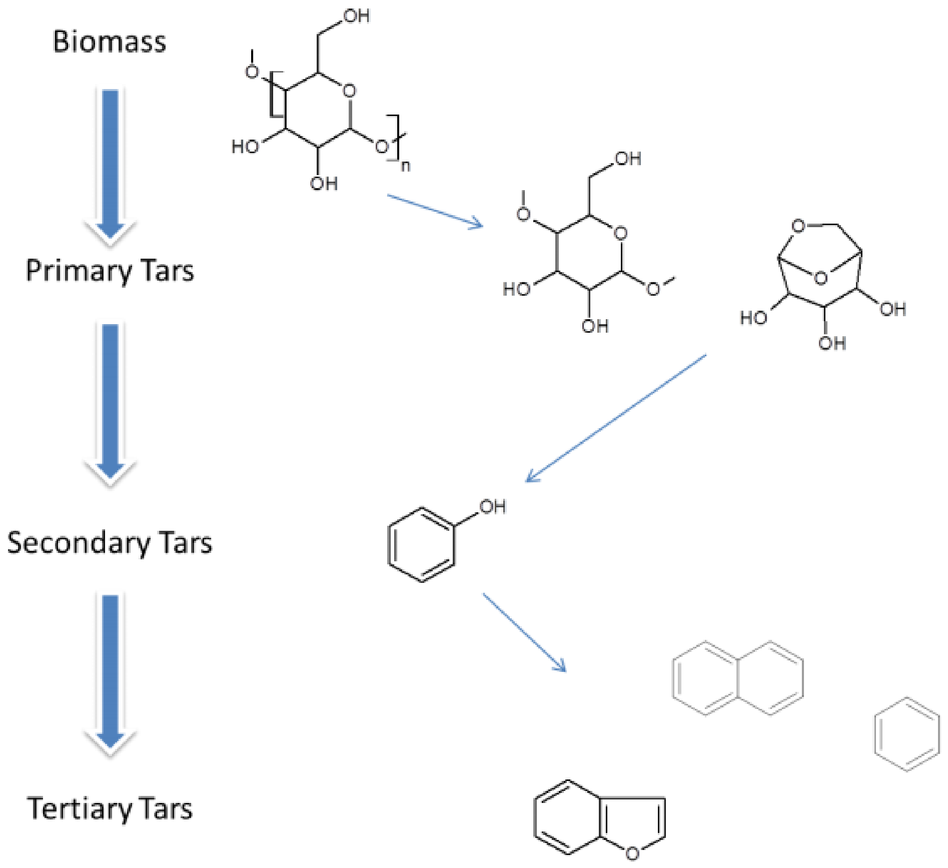

Figure 1 Tar compounds and classes as reported by (Milne et al., 1998). *Figure adapted from* (Devi et al., 2005).

An analysis of the formation of tar compounds showed that temperature is a key factor for the distribution of tars according to this characterization method. Three temperature dependent tar formation regimes can be identified in Figure 2. At lower temperatures (<600°C) the primary tars are totally dominant. At moderate temperatures (600-800°C) the secondary tars are formed. At high temperatures (>800°C) the primary tars are no longer visible and the main part of the tar will consist of the condensed tertiary tar compounds. Interesting to note is that the primary and tertiary tars are practically exclusive, i.e. the primary tars are destroyed before the formation of tertiary tars. Designing a tar removal system is thus highly dependent on the conditions in the gasifier as the tar configuration will depend heavily on it. It should however also be noted that the figure below states nothing about the quantity of tars, only of the relation between quantities of different types of gasifier tars in the product gas.

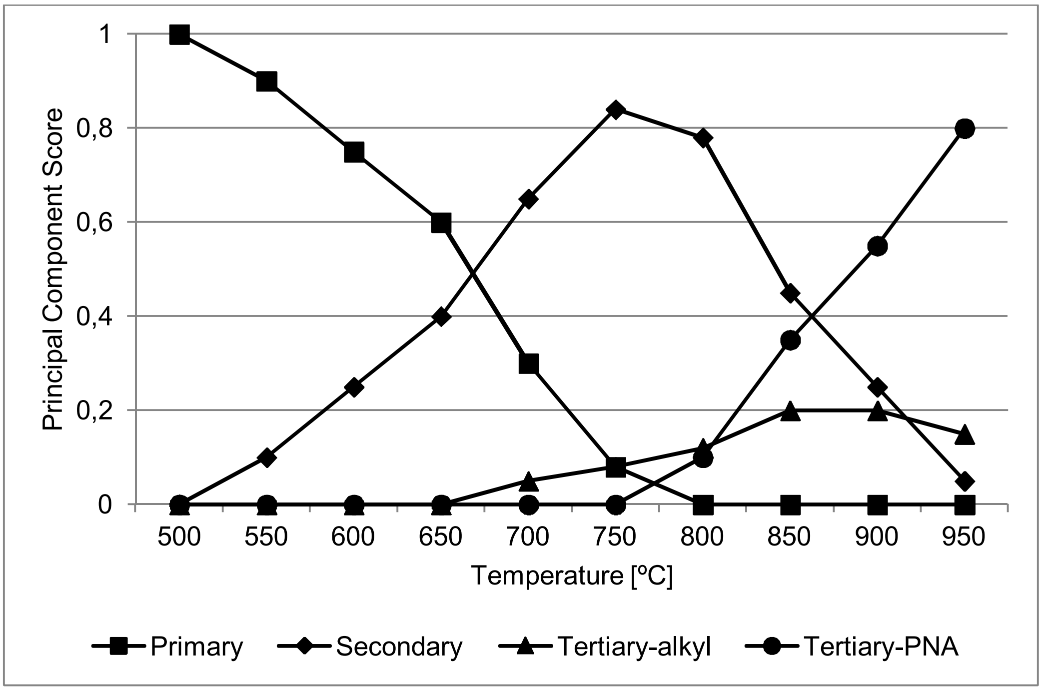

Figure 2 Tar product distribution. Adapted from (Evans & Milne, 1997)*.*

2.1.2 Tar removal

Many different approaches to the removal of tars from product gas have been investigated over the years. These approaches include as well mechanical and thermal as catalytic methods to eliminate or separate the tar from the product gas stream. Much work has also been put into limiting the formation of tars in the gasifiers to produce as clean a gas as possible. Several reviews of this research area have recently been presented (Anis & Zainal, 2011; Han & Kim, 2008).

An experimental setup for tar elimination in gas from a biomass gasifier similar to the one constructed within this project has previously been described (Van de Beld, Wagenaar, & Prins, 1997). The dutch company BTG constructed a Reverse Flow Catalytic Tar Converter (RFTC), a reverse flow reactor using a catalytically active bed of dolomite in two thirds of the reactor and bauxite as thermal buffers in the end zones. As other researchers have pointed out, the dolomite must be calcined to be active. When heating the reactor bed with flue gases, the oxides in the calcined dolomite, CaO and MgO, react with CO2 in the flue gas and thus lose their activity. However, it was shown that when the bed temperature increases to over 700°C the dolomite is recalcined and thus activated. At a flow cycle time of 40 minutes and a temperature of 1,050°C in the catalytically active part of the bed approximately 98% of the tar in the ingoing gas was converted, without affecting the heating value of the gas negatively. The wood gasifier to which the RFTC was connected was operated at sub-optimal conditions during these experiments with the intention of producing a gas with a concentration of tars (16.7-36.2 mg/Nm^3). Later publications (Espenäs & Frostäng, 1999; Fjellerup, Ahrenfeldt, Henriksen, & Gøbel, 2005) show that the dolomite in the RFTC was changed to a Ni-catalyst, which is known to be efficient for tar conversion but also suffers from high sensitivity to sulphur poisoning which was also recognized as a problem in the work. Further, the operating temperature of the system seems to have been decreased to about 900°C. Operating at lower temperatures not only decreases energy losses but it decreases the formation of soot from tars in the reactor, which has been shown to occur at high temperature tar conversion (Fjellerup et al., 2005).

2.2 Regenerative reverse flow processes

In a regenerative reverse flow process, heat is transferred between a fluid and a stationary phase. Usually streaming hot gas heats a bed of granular material, while the gas cools down. One of the most important parameters for the thermal buffer is the heat storage capacity and the mass of the solid packing material. The stored heat in the bed can be utilised by flowing cold gas in the opposite direction, heating the gas and cooling the bed. In contrast to recuperative heat exchanging, regenerative reverse-flow heat exchanging is a batch process. The reason for using such a device is the thermal efficiency that can be achieved, up to 95% (Matros & Bunimovich, 1995). This is partly due to the large heat transfer area that can be obtained in a bed of granular material, partly to the high heat transfer coefficients that can be obtained in a packed bed with a proper choice of grain size and gas flow rate. A recuperative heat exchanger seldom exceeds 80% in thermal efficiency due to technical-economical reasons. Thus the regenerative reverse flow reactor systems may be a better choice when heat integration is a crucial aspect of process design, although the reactor system setup is more complicated than an ordinary fixed bed reactor. An in-depth description of reverse-flow reactors, their applications and operation have been published earlier (Matros & Bunimovich, 1996).

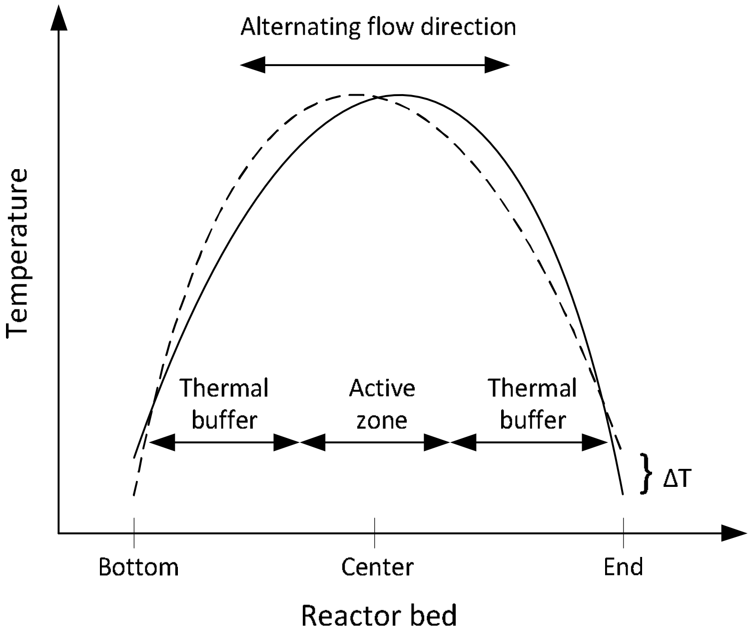

Figure 3 The alternating temperature profiles of the reactor bed in a reverse flow process

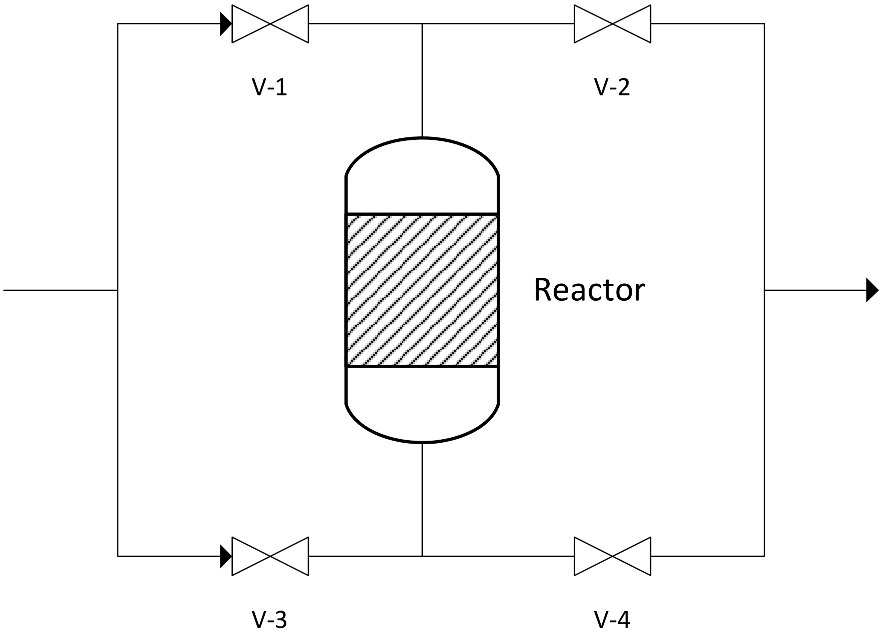

Figure 4 The basic valve scheme of a reverse flow reactor setup. For downward flow the vents V-1 and V-4 are open whereas V-3 and V-2 are closed. Switching all vents simultaneously changes flow direction.

The first regenerative reverse flow process was developed in the 1930’s for a total oxidation of hydrocarbons using alternating flow direction where the process heat was shuffled back and forth between two regenerative buffers. The reaction was completed, by homogenous reactions in the hot gas phase, in the hot zone in between the two heat exchangers. Today this process is named Regenerative Thermal Oxidation (RTO) and is still used in volatile organic compounds (VOC) abatement (Matros & Bunimovich, 1995). The RTO concept was developed further by combining it with a centrally placed oxidation catalyst, creating the Regenerative Catalytic Oxidation process (RCO) (Boreskov & Matros, 1983). The RTO and RCO of VOC have proven its usefulness in industrial operations and today a lot of engineering companies offer commercial plants for sale.

Further, due to the possibility of achieving high thermal efficiency, the regenerative reverse flow concept has been used in several industrial processes, except for the VOC abatement. Catalytic oxidation of SO_2, selective catalytic reduction of NO_x, methanol synthesis and partial oxidation of methane for syngas production are processes which have all been studied using reverse flow systems (Van de Beld et al., 1997). All these processes are exothermic which has been the traditional application of this type of system. It has however also been shown that the concept can be applied to endothermic reactions, such as dehydrogenation of ethylbenzene (Haynes, Georgakis, & Caram, 1992). Tar cracking, which is endothermic, supported by an exothermic partial combustion was the first reported reaction scheme utilizing a reverse flow process setup (Van de Beld et al., 1997).

As mentioned earlier, this project builds on work with POX of methane which was studied in an earlier project. Modelling of the reverse flow reactor system showed that when reforming methane, very high efficiencies are possible even in high temperature POX applications. The problem with producer gas from biomass gasification is the high amounts of lower hydrocarbons and tars and high temperature POX applications as elevated levels of soot is formed from the lower hydrocarbons and tars when the gas is heated to high temperatures. Earlier work (Svensson, Tunå, Hulteberg, & Brandin, 2012) has shown high levels of soot at elevated temperatures for these gas mixtures. A pre-reformer that reforms lower hydrocarbons and tars placed before a methane reformer reduces the soot formation at POX temperatures. If the desired product after gasification is synthetic natural gas (SNG) then it is advantageous to keep the methane in the gas and synthesis the syngas components, rather than reforming methane and then synthesising it again.

This work builds on this principle, convert all hydrocarbons, including tars with the exception of methane into syngas. The reverse flow operation should prove beneficial here as well as for methane reforming, even though methane reforming requires more energy as there is more methane than other hydrocarbons in the producer gas. Due to the higher energy efficiency of reverse flow operations, less oxygen would be required per unit of raw producer gas, thus reducing operating and investment cost. The use of a bed material with catalytic activity for tar reforming, that does not suffer from sulphur poisoning, will further increase the robustness of the system.

2.3 Oxidation of ammonia by nitrogen oxides

Apart from tars, another contaminant present in the gas from a biomass gasifier is ammonia (NH_3). The ammonia in the producer gas is a product of the gasification process as the nitrogen which is an integral part of proteins and other compounds which constitute the biomass reacts with hydrogen to form ammonia. Gasifier design and process parameters affect the ammonia formation, but the producer gas contains from a few hundred ppm up to a few percent ammonia (Torres, Pansare, & Goodwin, 2007), with typical values being in interval of 1,000-5,000 ppm (Xu, Donald, Byambajav, & Ohtsuka, 2010). The fuel-bound nitrogen may react to produce other species, mainly nitrogen gas (N_2), but also hydrogen cyanide (HCN), nitrogen oxides (NO_x and N_2O) and isocyanic acid (HNCO) at lower concentrations (Zhou, Masutani, Ishimura, Turn, & Kinoshita, 2000). Volatile nitrogeneous species, such as NH_3, HCN and HNCO, are precursors for NO_x formation in downstream gas combustion. The permitted emission level for ammonia is lower than for NO_x, so there is a high demand for ammonia removal. As NO_2 is a highly corrosive gas, consideration must also be given to the effect on equipment and materials if NO_2 is produced from ammonia. Further, if the producer gas is not intended for combustion, but rather for synthesis operations, e.g. liquid fuel synthesis, ammonia is a potential poison to synthesis process catalysts.

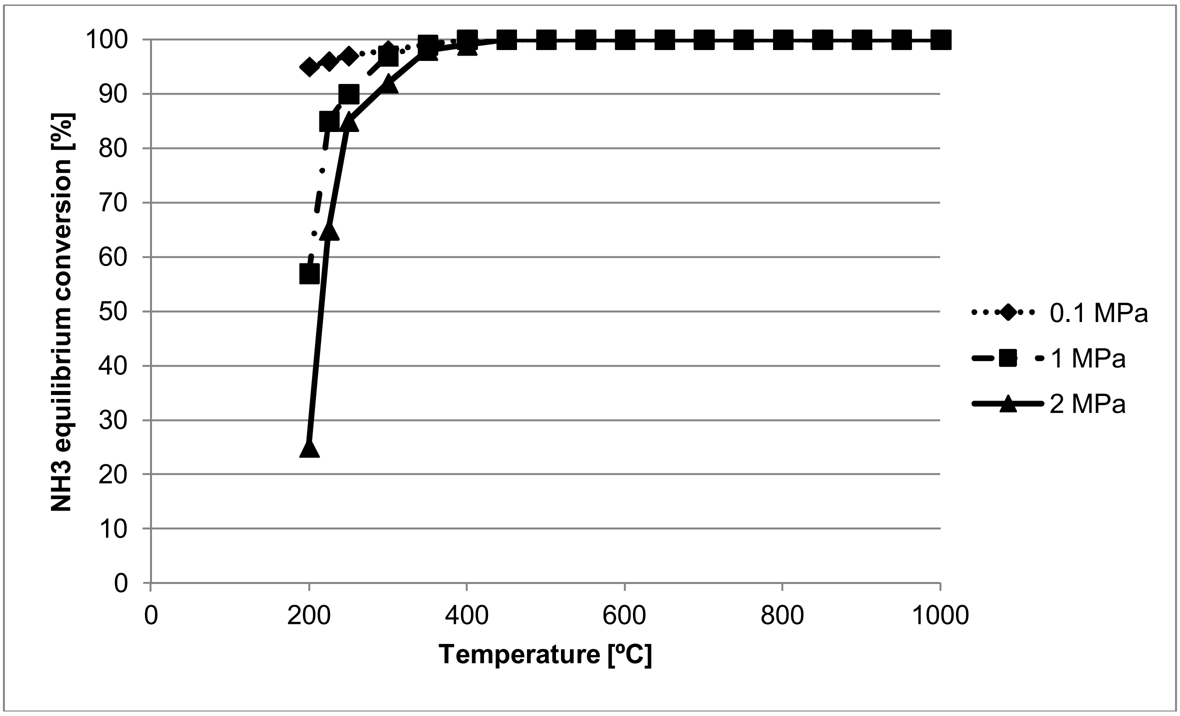

Figure 5 Conversion of ammonia in thermodynamic equilibrium at different pressures in a producer gas from biomass gasification. Figure adapted from Torres, Pansare, & Goodwin (2007).

As has been shown earlier (Torres et al., 2007) ammonia is not stable at the temperature (700-1,000ºC) and pressure (1-15 bar) after the gasification step. In thermodynamic equilibrium the ammonia in this environment decomposes to nitrogen and hydrogen, which is shown in Figure 5. The ammonia content in the producer gas is thus due to kinetic limitations in the decomposition reaction, which is shown below.

$$2\,NH_3 \rightarrow N_2 + 3\,H_2 \qquad \text{Eq. 1}$$

This means that the reaction is to slow to eliminate the ammonia at the actual temperatures, pressures and residence times. The rate of reaction can, however, be accelerated by a suitable catalyst. If a catalytic reforming unit is used the ammonia is reformed parallel to the hydrocarbon reforming. For plants without catalytic reformers, the ammonia will remain in the gas.

Removing the ammonia from gas requires either a physical or chemical approach. A typical physical is a water scrubber. If the gas is scrubbed in a water scrubber, the ammonia will just be move to another location - it will not remove the problem and the ammonia needs to be neutralized by an acid. Removing ammonia using a water scrubber will also have a severe impact on the energy efficiency of the gasification process as the producer gas has to be cooled to a very low temperature for the scrubbing operation and then reheated for synthesis operations.

Initially, the intention was to include oxidation of ammonia in the producer gas using NO_2 with a new method developed by the research team (Tunå & Brandin, 2013) called reverse selective catalytic reduction (SCR). SCR is a process common to heat and power plants to eliminate NO_x from flue gases. In SCR ammonia reacts with NO_x over a catalyst forming N_2 and H_2O according to the reactions below.

$$4\,NO + 4\,NH_3 + O_2 \rightleftarrows 4\,N_2 + 6\,H_2O \qquad \text{Eq. 2}$$

$$6\,NO_2 + 8\,NH_3 \rightarrow 7\,N_2 + 12\,H_2O \qquad \text{Eq. 3}$$

This reaction requires oxygen that is not present in the synthesis gas. Without oxygen the reaction stops. Adding oxygen to the synthesis gas would not only remove the ammonia but also a portion of the hydrogen in the gas thus also increasing the temperature of the gas (Leppalahti, 1999). There is also a reaction (4) known as fast SCR in which NO and NO_2 reacts with ammonia to form N_2 in the absence of oxygen. The fast SCR kinetics is much higher than the standard SCR reaction. In this reaction a ratio of 1:1 for NO_2:NO yields the highest conversions (Brandin, Andersson, & Odenbrand, 1989).

$$NO + NO_2 + 2\,NH_3 \rightleftarrows 2\,N_2 + 3\,H_2O \qquad \text{Eq. 4}$$

All the SCR-units in operation are operating with oxidizing gases, i.e. gases containing oxygen and nitrous oxides. Producer gas is the opposite with a high content of hydrogen and the pollutant being ammonia instead of nitrogen oxides. Thus, the proposed process was to run a reverse SCR in which nitrogen oxides are injected into the producer gas stream and reacted with ammonia over a suitable catalyst.

2.4 Combined tar reforming and selective ammonia oxidation

Since the temperature in the reverse flow reactor ranges from 250 °C at the inlet to over 700 °C in the centre, it should be possible to put a catalyst as a slab at a suitable location. The plan was to put the SCR catalyst in the reverse flow reactor at a position that would put it at the appropriate temperature at all times. This idea was a good idea in theory but there are several complications that led to this idea being rejected. First of all, the packing material of the reverse flow reformer, dolomite, has different material properties than the SCR catalysts. This could lead to a crushing of the SCR catalyst pellets as the dolomite expands because of the high temperature. Secondly, it would be near impossible to load the catalyst into the reactor and keep it as a slab, while flipping the reactor over to fill the oxygen inlets at the top. Without a near perfect slab, parts of the gas could go through the reactor without reaching the catalyst or the catalyst could be exposed to too high or low temperatures, making it ineffective at selective oxidation. Thirdly, the reactor would have been even more complicated to build to ensure a good distribution of NO_X in the bed before the catalyst slab. Lastly, the exit temperature of the reverse flow reformer is almost at the same temperature that the vanadium based SCR catalyst operates at and with high temperature valves the gas could be introduced directly into the ammonia removal reactor without any pre-heating/cooling. Due to these reasons the plans for a combined tar reforming and selective ammonia oxidation setup were rejected.

3 Experimental setup

3.1 The reverse flow pre-reformer reactor and apparatus design

The reformer is built using a Sandvik 253 MA high temperature steel tube, six inches in diameter and 0.7 meters long. Five smaller tubes measuring 13.7 mm in diameter are inserted into the reactor tube, four for oxygen injection and one centred as a thermocouple pocket. The thermocouple pocket is open to the outside and welded shut in the reactor centre. The four oxygen tubes are connected in a manifold at the ends of the reactor. The reactor is symmetrical on both ends which is necessary for reverse-flow operation. A filler tube is located at the top of the reactor to allow filling of bed materials. The reactor is shown in Figure 6.

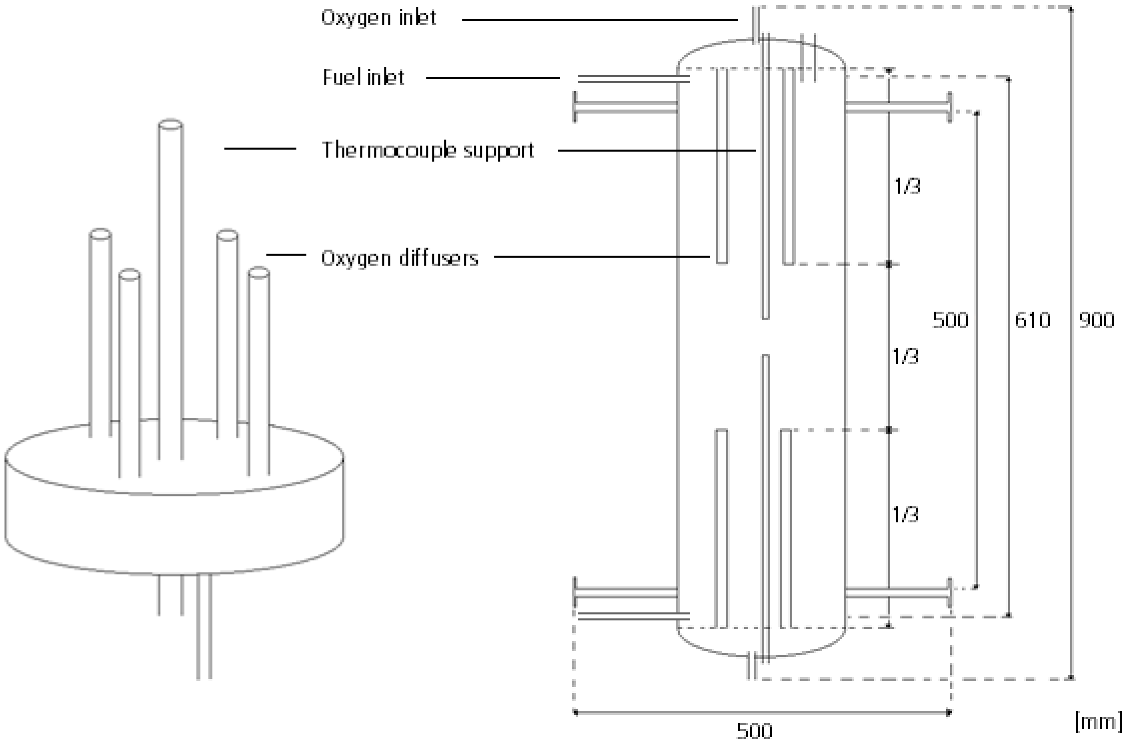

Figure 6 Illustration of the reactor unit (right) and the oxygen diffusers (left), which are located in the top and bottom part of the reactor.

Process gas inlets are 0.75 inch steel tubing connected to four electromagnetic valves. An additional three-way valve is used for oxygen flow direction control. Gases are fed using mass flow controllers and water is fed using a pump. Methylnaphthalene is injected by means of a syringe pump, see Figure 7. O_2 is injected in the middle of the reactor in separate tubes.

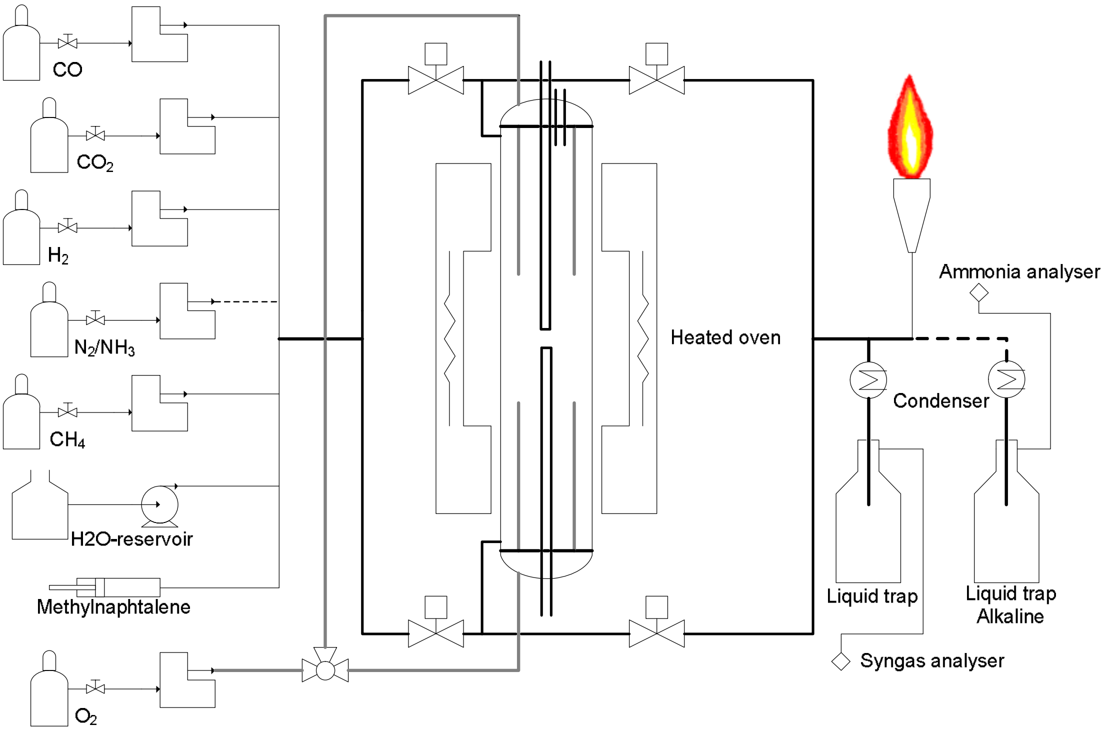

Figure 7 Schematic of the laboratory setup of the reverse-flow tar cracker.

As can be seen in Figure 7, a flame is present. The flame colour acts as an indication of a few properties of the gas. Uneven volume flow will be clearly visible by different flame heights and any hydrocarbon with C-C bonds will burn yellowish in colour. A flame with only CO, H_2 and CH_4 will have a faint bluish colour. This gives a rough indication of the performance of the reformer without time consuming and expensive chemical analysis. Flame indication is no substitute for a thorough analysis, but operating conditions that gives yellow flames can be ignored when choosing conditions for further analysis.

Figure 8 is a picture of the reverse-flow tar cracker in the laboratory. It is not possible to see the actual reactor tube due to the thick insulation around the reactor. All tubing on the inlets and outlets of the reactor is insulated.

Figure 8: Laboratory reactor with mass flow controllers, flame cage and analysers.

The reactor is filled with dolomite in a fraction of around 1-3 mm, the dolomite particles are shown in Figure 9.The small size of the bed material was chosen to ensure as large surface area as possible, to have as small volume between particles as possible and to have the lowest possible pressure drop in the reactor. Smaller particles would increase the surface area but it would also increase the pressure drop. The volume between the particles is critical due to the fact that when sufficient volume is available, a flame can be formed which can lead to explosions when O_2 is mixed with H_2. Minimizing the void between the bed particles is therefore important in this type of reactor.

Figure 9 Dolomite particle size, the scale is in cm.

All tubing from gas mixing to the flame is heated stainless steel tubing. After the mixing the gas and water is led through a tube on the outside of the reactor, heating the mixture, evaporating the water and cooling the reactor inlet. The outlet of the reactor goes to a burner, but a part of the gas flow (about 2 Ndm^3/min) goes to the syngas analyser. This device features an IR-sensor for CO, CO_2 and CH_4. A TCD is responsible for the H_2 reading in the analyser. NH_3 analysis is a cold analysis and thus all the water that condenses will need to be removed prior to analysis, without losing NH_3 to the water. The liquid trap in Figure 7 contains a strong alkaline solution (9 M NaOH) that will not absorb as much NH_3 as pure water would. When NH_3 is analysed, the NH_3 analyser takes an additional 2 Ndm^3/min of gas.

The reactor is insulated with ceramic half shells, the shells in the middle have heating elements inside allowing heating of the reactor. When the temperature inside the reactor is sufficient (above 200 °C), methanol is injected instead of water along with H_2 and N_2. O_2 is added to this mixture which increases the temperature in the reactor until operating temperature is achieved. When operating, methanol injection is shut off and a model synthesis gas is used instead. During operation, the amount of O_2 is reduced from the stoichiometric 1.0 to 0.3-0.4 depending on operating conditions such as temperature, flow and heating value of the gas etc. By using two oxygen inlets (four tubes on each inlet), two hot zones are created that will increase in temperature when active. Only one of the O_2 inlets, the one closest to the current raw gas inlet, is active at the same time, which will raise the temperature in the active zone. When flow direction is reversed, O_2 is shut off at the inlet the temperature will decrease due to endothermic reforming reactions, heat transfer to the reactor ends and heat losses. At the same time the other zone becomes active and the temperature there will increase due to the O_2 addition. In

Figure 10 this is visible as the temperature in the left part of the middle is lower than the right part.

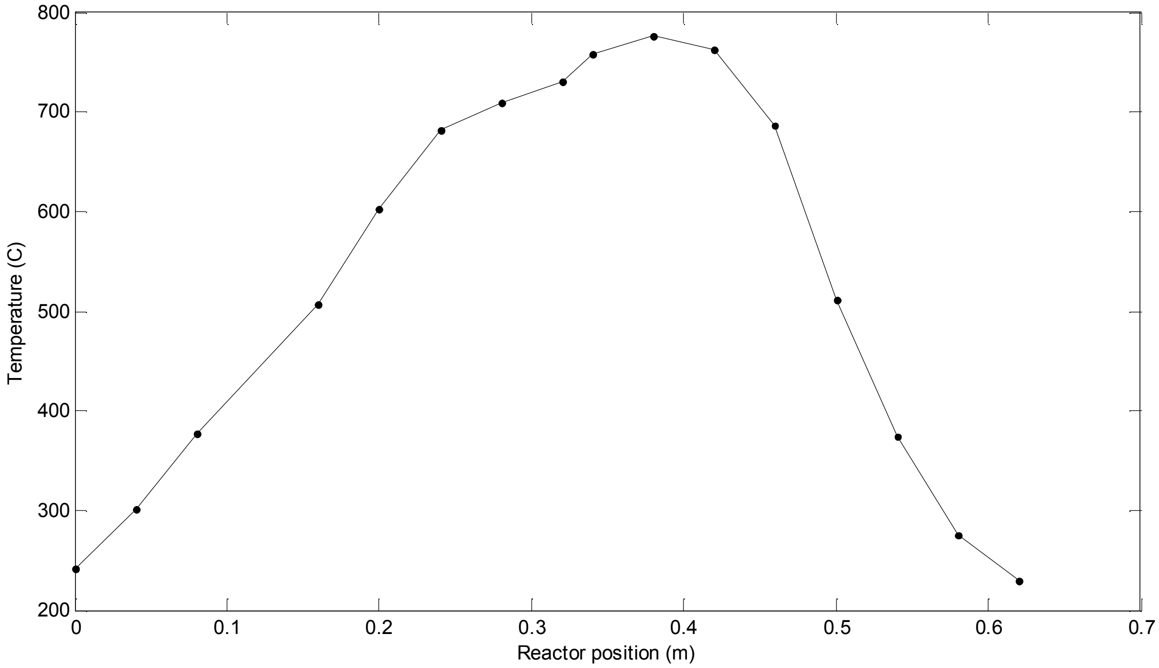

Figure 10 Typical temperature profile in the reactor during experiments.

Oxygen inlets are located approximately at 0.24 and 0.42 meters. Due to mixing problems in the bed and O_2 inlet flow characteristics, the O_2 is not consumed instantly. When looking at Figure 10 and assuming that flow direction is from left to right, the temperature will increase in the three points left of the middle. The largest increase will be in the left most point of the three. The temperature in the centre of the three will increase more than the right. The temperature at the ends of the reactor will increase/decrease as flow direction changes. The active inlet will be cooled down by the incoming gases that are kept at 165 °C because of valve limitations. The active outlet will be heated by the exiting gas that transports heat from the centre of the bed towards the outlet. It was deemed desirable to keep the end points below 300°C to avoid unnecessary heating of the outlet valves.

Flow direction is changed by the valves over and under the reactor in Figure 7. Only one of the valves above the reactor is open at any time and the same applies to the lower valves. An operation in which only the upper or the lower valves, but not both, are open at the same time is denoted *bypass* and is used for measuring the inlet concentration of species. This means that both reacted and unreacted gases flows through the same tubing, eliminating tubing as a possible source of errors in concentrations due to condensation, absorption etc.

In Table 1 is listed the inlet composition used during experiments. The experiments were performed at atmospheric pressure. Pressure drops over the reactor ranged from 15-90 mbar depending on temperature and volume flow. For the NH_3 experiment, bottled NH_3 in N_2 with a concentration of 5,000 vppm was injected to give a total concentration of NH_3 of 2,500 vppm at the mixing point. 2,500 vppm was never measured by the analyser but a concentration of 1,400 vppm was measured at the outlet when the reactor was bypassed. The reason that 2,500 vppm are not measured is because ammonia sticks to all metal surfaces on the apparatus. It would take hours for the system to be saturated with ammonia after which almost all ammonia could measured.

Table 1 Gas composition in inlet during reverse flow pre-reforming experiments.

Component	**Gas fraction**
CO	25 vol-%
CO_2	15 vol-%
H_2	25 vol-%
CH_4	10 vol-%
H_2O	25 vol-%
1-Methylnaphtalene	15,000 mg/Nm^3

3.2 Selective ammonia oxidation setup

Ammonia cracking is another chemical method that works similar to hydrocarbon reforming. The reverse-flow reformer should be able to reduce the level of ammonia in the gas but it will not be able to convert all of the ammonia.

All the SCR-units in operation are operating with oxidizing gases - containing oxygen and nitrous oxides. Synthesis gas is the opposite, having a high amount of hydrogen and with the pollutant as ammonia instead of nitrous oxides. It is well known that NO_X is reduced by CO and H_2, for instance CO is oxidised to CO_2 and NO_X to N_2 over three-way catalysts in automotive applications. Hydrogen can be used to reduce NO_X over precious metal catalysts at low temperature. If the injected nitrogen oxides are not reduced the gas gets polluted by nitrogen oxides instead of ammonia. In order to determine if the nitrous oxides are reduced over the catalyst, experiments were run without ammonia in the gas. The nitrous oxide levels were measured as a total NO_X-level using two different types of Dräger short-term tube 2-100 and 100-5,000 ppm NO_X. Gas composition for the experiments is presented in Table 2 and can be considered a simulated gas after an air-blown gasifier with the exception of water. Water is excluded due to analysis problems.

Table 2 Gas composition during selective ammonia oxidation experiments.

Component	**Fraction**
N_2	65 vol-%
CO_2	11 vol-%
CO	13 vol-%
H_2	11 vol-%
NO_X	2,000 vppm

The gas composition for the experiments is listed in Table 2 with the addition of 2,000 ppm NH_3. CO, CO_2 and H_2 are fed to the reactor along with a stream of 5,000 ppm NH_3 in N_2. No water is present in the experimental gas as it would condense and capture the ammonia thus giving a lower measured amount. The lack of water in the gas will affect the equilibrium for some reactions such as the Boudouard reaction. The effect of water in SCR is limited (Odenbrand, Gabrielsson, Brandin, & Andersson, 1991). At higher temperatures lower amounts of ammonia was measured which could indicate dissociation of ammonia according to reaction (1).

The NO_2 is injected as a mixture of 1 vol-% NO_2 in N_2. The feed gas flow was 1.6 Ndm^3/min and the added N_2/NO_2 contributed with an additional 0.4-0.5 Ndm^3/min depending on stoichiometry. Two different SCR-catalysts were tested in the experiments; a V_2O_5 based catalyst and a H-mordenite catalyst. GHSV for the vanadium catalysts was 210,000 h^{-1} and for the H-mordenite 75,000 h^{-1}.

4 Results and discussion

The purposes of the tar reformer/pre-refomer is to be able to convert tars, not convert methane, convert at least a part of the ammonia in the gas and do so as energy efficiently as possible without using a nickel based catalyst. Energy efficiency is achieved by the reverse-flow operation that will allow high temperatures in the reactor centre thanks to the efficient heat exchanging possible. Table 3 presents the conditions for the experiments as well as the results such as tar analysis, and gas composition in the outlet.

Table 3 Tar conversion at three residence times and two temperatures.

Experiment	**1**	**2**	**3**	**4**	**5**	**6**
Reactor inlet data						
Flow [Nm3/h]	0.51	0.85	1.2	0.51	0.85	1.2
GHSV [h^{-1}]	44.8	74.8	105.3	44.8	74.8	105.3
Residence time [sec]	29	17	12	29	17	12
Pressure drop [mbar]	13	39	87	13	39	87
1-Methylnaphthalene [mg/Nm^3]	15,050	15,050	15,050	15,050	15,050	15,050
Target temperature [°C]	700	700	700	800	800	800
Outlet tar content						
Total tar [mg/Nm^3]	7,160	6,520	6,210	5,900	7,820	7,010
Benzene[mg/Nm^3]	145	623	503	347	732	566
Toluene[mg/Nm^3]	85	233	182	215	252	227
Naphthalene[mg/Nm^3]	5,820	4,130	2,750	4,520	4,970	3,460
1-Methylnaphthalene[mg/Nm^3]	1,120	1,540	2,780	820	1,870	2,750
1-Methylnaphthalene conversion	93%	90%	82%	95%	88%	82%
Total tar conversion	52%	57%	59%	61%	48%	53%
Outlet gas composition (dry)						
CO in outlet [vol-%]	10	27	28	9	26	28
CO2 in outlet [vol-%]	22	30	41	30	39	42
H2 in outlet [vol-%]	57	36	27	55	26	26
CH4 in outlet [vol-%]	16	12	9*	16	12	9*

*For the higher flow, the mass flow controller for CH4 was limiting and the concentration was set to 8 vol-%

Interestingly, at higher flow rates the conversion of 1-methylnaphtalene goes down but the total tar conversion does not. It is very probable that the reactor would have been able to handle higher flow rates, but no mass flow controllers were available to handle those flow rates. The space velocities listed are much lower than for conventional catalytic reformers. In Table 4 is presented the necessary dimensions of reactor able to handle the flow from the 10 MW Milena gasifier of 2,750 Nm^3/h. The radius/length ratio was kept constant and the same as the experimental reactor.

Table 4 Scale-up volume of the reverse flow pre-reformer, a space velocity of 263 h^{-1} translates to a flow of 50 Ndm^3/min for the experimental reactor.

GHSV (h^{-1})	44.8	74.8	105.3	263.3
Radius (m)	1.3	1.1	1.0	0.7
Length (m)	10.9	9.2	8.2	6.0
Volume (m^3)	61.4	36.8	26.1	10.4

4.1.1 Bed packing issues

Filling the reactor with bed material is a critical step in preparing the experiments. The reactor needs to be flipped over several times to allow the O_2 inlets in the top to be equally filled. If the inlets are not equally filled, the tubes with the least material in them will have a lower pressure drop and will therefore have a higher flow. A higher flow in one or two of the tubes will result in an uneven O_2 distribution in the reactor cross-section. This can lead to several problems such as severe hot-spots, channelling of the O_2 if the flow profile is laminar. Channelling may allow the O_2 to remain in the gas long enough to heat up unwanted parts towards the outlet and in worst case to mix with the syngas at the outlet. Problem with the filling was experienced during the experiments. When heating up there was incomplete conversion of the fuel when flow direction was from the top to the bottom. Flowing from the bottom to the top resulted in almost complete conversion of the fuel.

4.1.2 Tar cracking performance

The performance of tar cracking in the reverse-flow pre-reformer is evaluated at three different space velocities for two temperatures. The temperature at the ends of the reactor was kept below 300 °C at all times.

As can be seen in Table 3, more than 50% of the total tars are converted. Over 80% of the 1-methylnaphtalene is converted, although in the case with the lowest residence time there is approximately the same amount of naphthalene as there is 1-methylnaphtalene. The target temperature was approximately 700°C in the active reaction zone for experiments 1, 2 and 3 while for experiment 4, 5 and 6 the target temperature was 800°C. The target temperature is the highest temperature in the reactor at the point where the active oxygen inlets are. For all experiments, only small amounts of benzene and toluene remain in the gas.

4.1.3 Gas composition

Preserving the methane in the gas while cracking tars and lower hydrocarbons will have two benefits. If the production is synthetic natural gas, it is important to have as much methane in the gas from the gasifier as possible, as that will reduce the need for downstream methanation. Methanation is an exothermic reaction that will reduce the available energy in the desired product. Secondly, methane reforming is a very energy intense process that requires high temperatures. Lower hydrocarbons and tars will form soot at higher temperatures. It is therefore preferable to first remove the tars and lower hydrocarbons in one reactor and then do methane reforming in another. This also has a benefit that sulphur removal can be achieved after the pre-reformer where organic sulphur would have been harder to remove. Sulphur as H_2S is readily removed by the use of ZnO-beds, whereas organic sulphur may not. Figure 11 presents the concentrations of the most important species in the inlet and outlet of the reformer for a residence time of 29 seconds (see Table 3 for comparison between residence times).

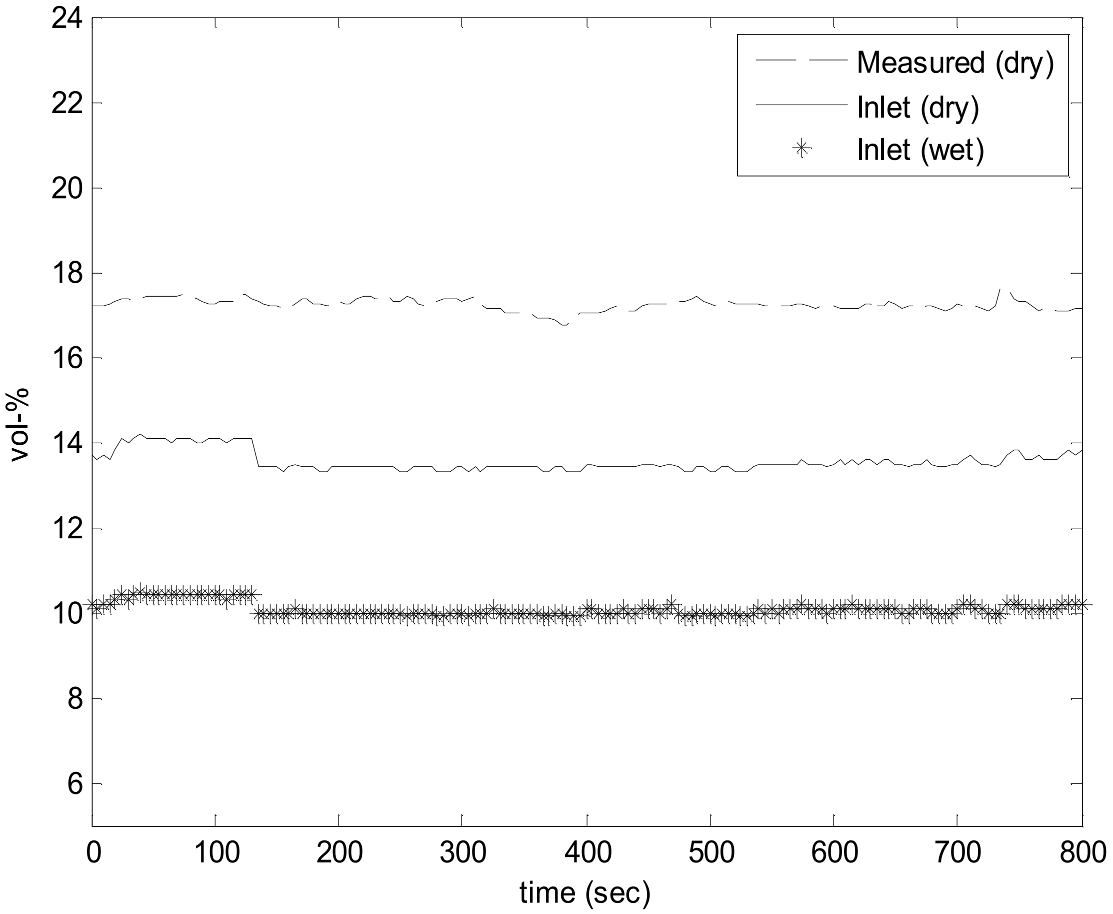

Figure 11 Concentrations of CH_4 at the inlet (controlled by mass flow controllers) and outlet (measured with an IR analyser).

There is interference on the CH_4-signal from other hydrocarbons in the gas, but the amount of CH_4 in the gas is at least as much at the outlet of the reformer as there is in the inlet. Any extra CH_4 comes from cracking of the tars.

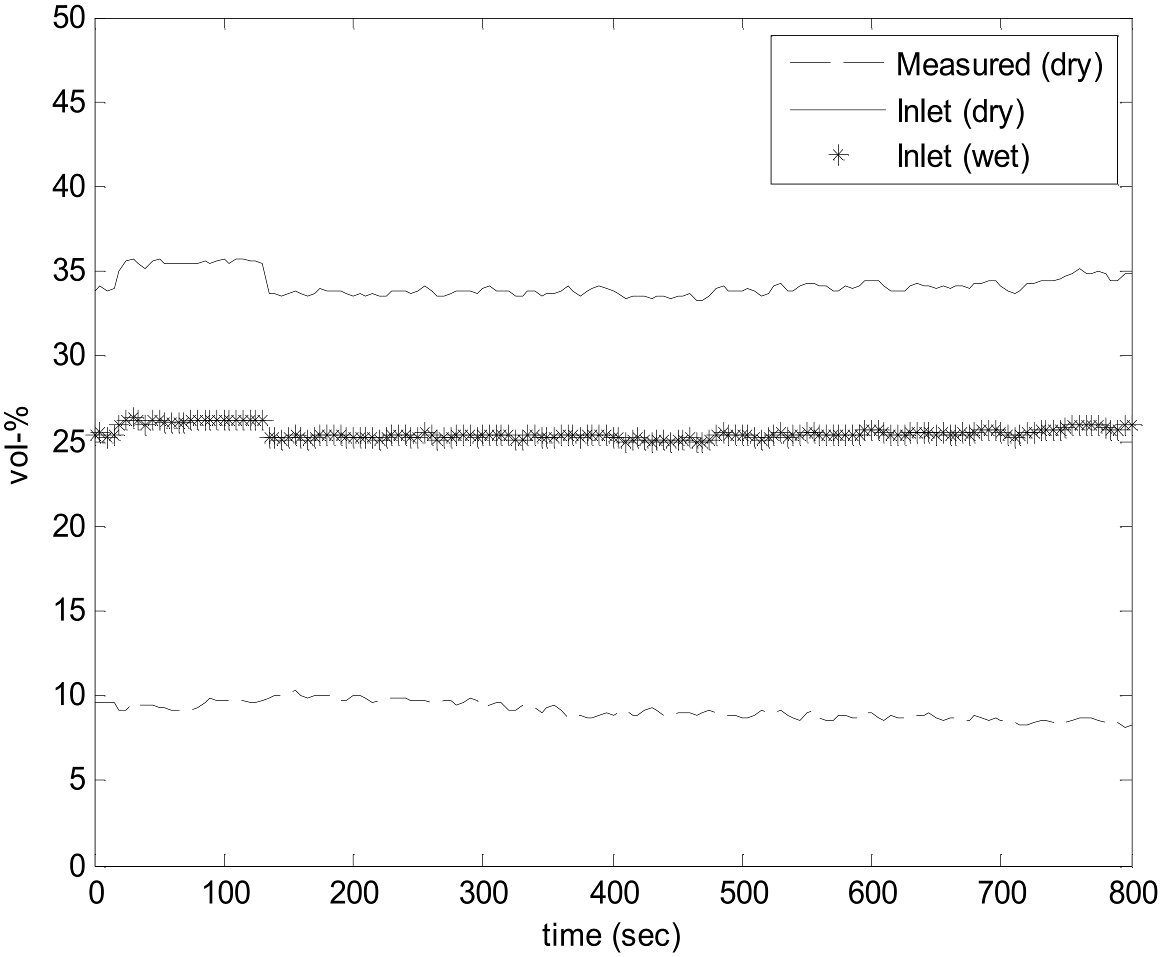

Figure 12: CO concentrations at the inlet and outlet during experimental run (measured with IR analyser).

The low concentration of CO in the outlet is an effect of water-gas shifting as the equilibrium is pushed towards H_2 at low temperature. A higher temperature at the reactor ends would be desired to decrease the H_2:CO ratio and yield a more favourable ratio of 2-3:1 for downstream synthesis.

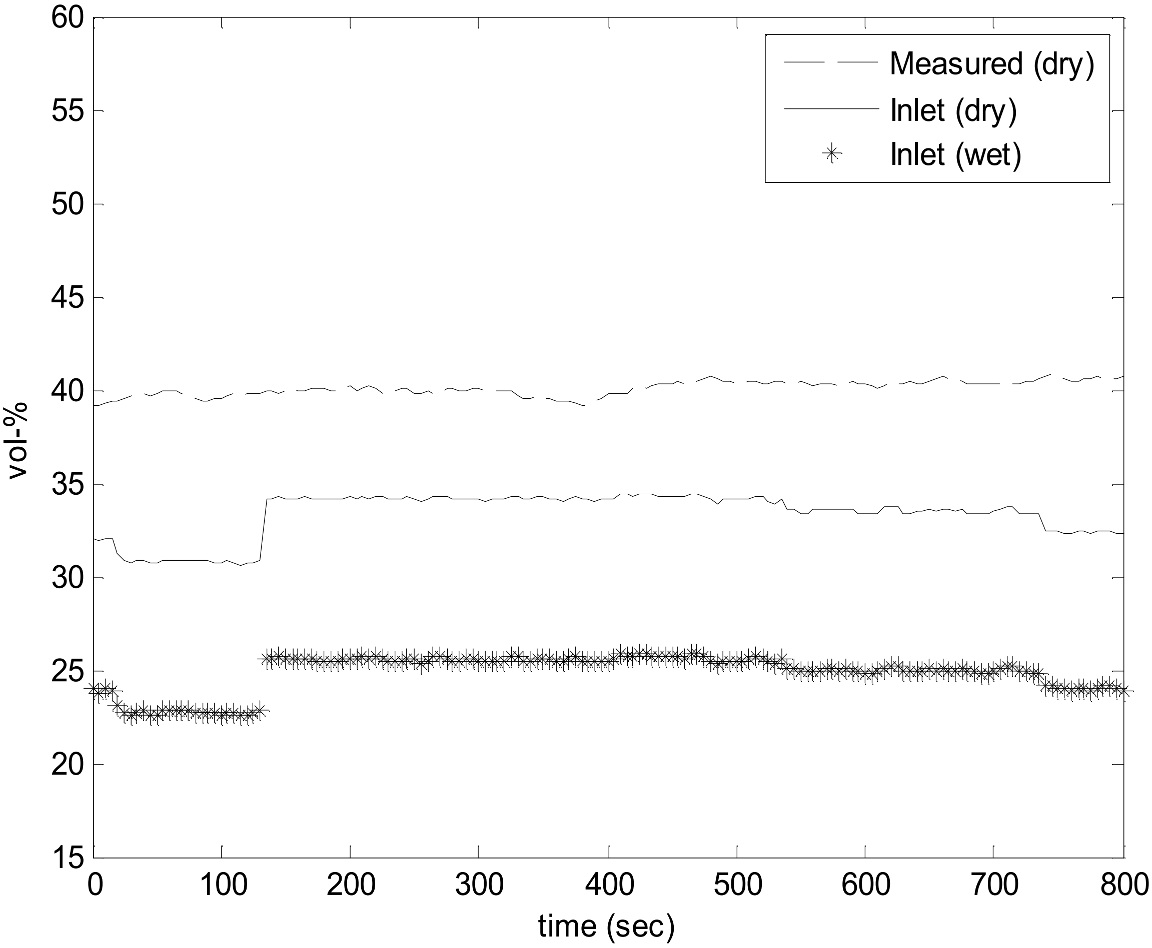

Figure 13: H_2 concentration at the outlet and inlet (measured with TCD detector).

H_2 concentration is the inverse of CO concentration as the water-gas shift reaction produces H_2 when consuming CO.

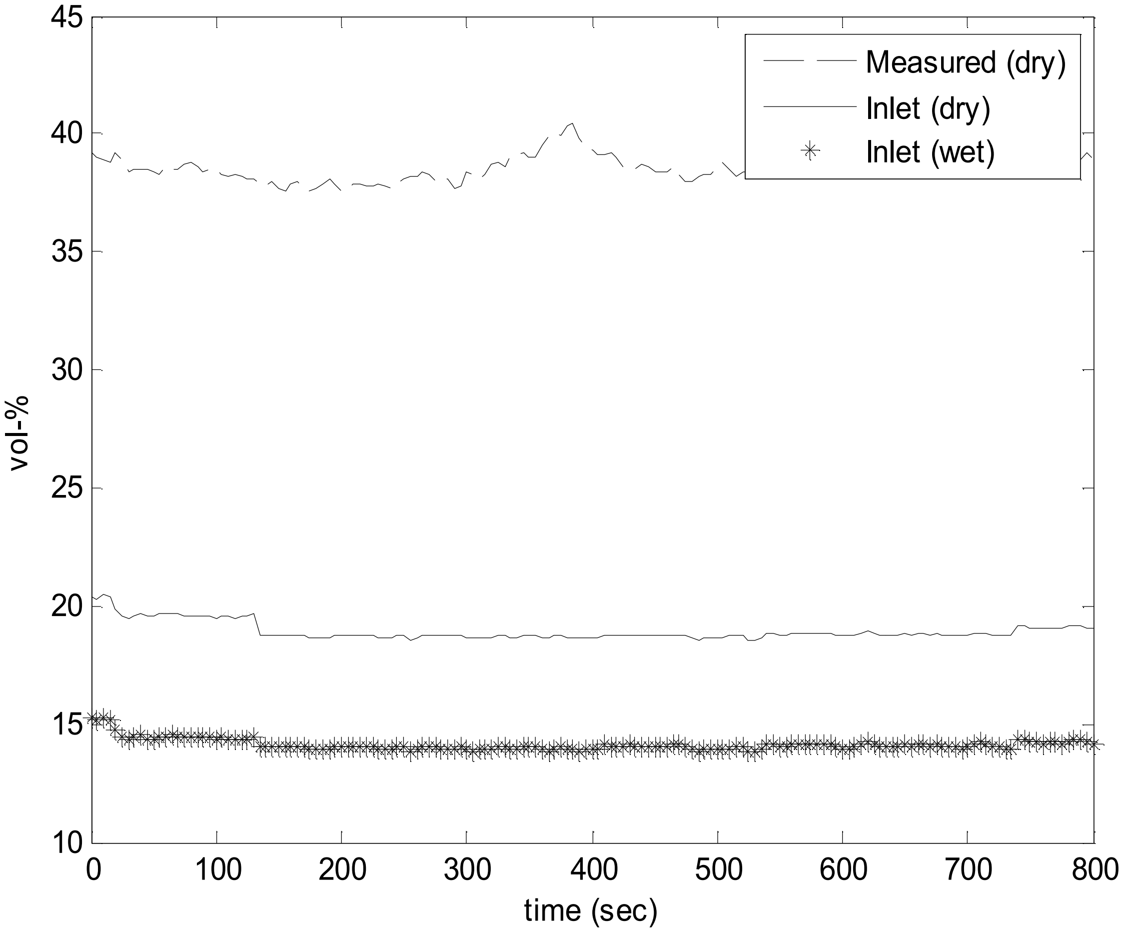

Figure 14: Concentration of CO_2 in the inlet and outlet during experimental run (measured with an IR analyser).

The CO_2 concentration follows the H_2 concentration as the gas is equilibrated towards the ends of the reactor with more CO_2 and H_2 at the outlet.

Figure 15 shows the equilibrium concentrations of the species in the gas. At the time of measurement of the data in Figure 11, Figure 12, Figure 13 and Figure 14, the outlet temperature was 290 °C. Comparing the equilibrium composition in Figure 15 with the measured composition indicates a gas approaching equilibrium. The measured concentration of H_2, CO and CO_2 is at 40, 10 and 35 vol-% (dry) respectively and the dry equilibrium concentrations are 52, 7 and 40 vol-%. It should be noted that uncalcined dolomite will release CO_2, thus pushing the equilibrium towards more CO and less H_2. This makes any comparison against theoretical equilibrium calculations difficult.

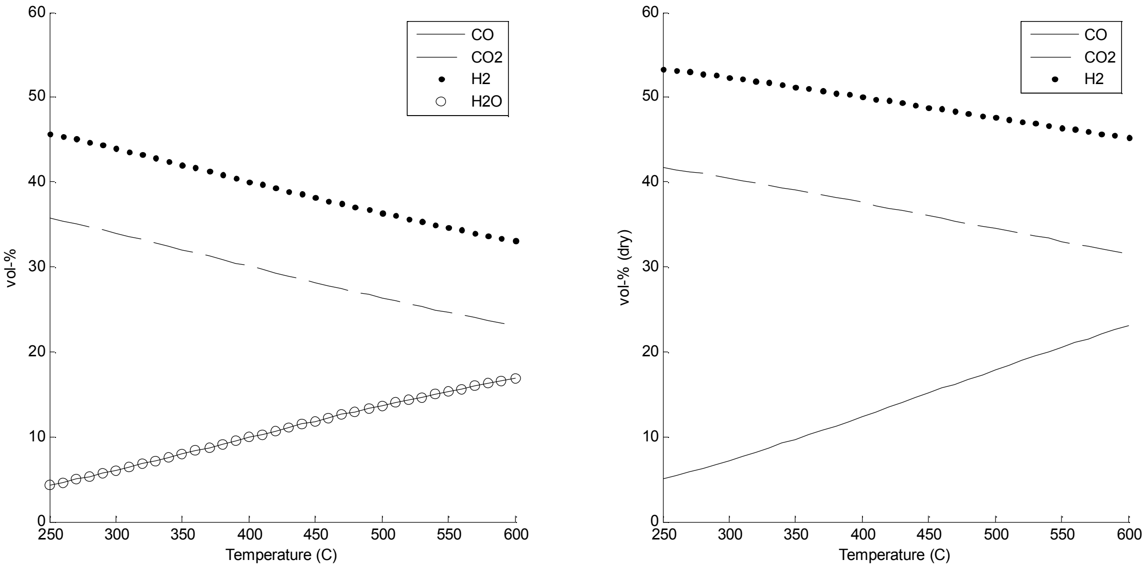

Figure 15 Water-gas shift equilibrium of the model gas as a function of temperature for wet and dry gas.

The problem with this shift activity is that the H_2:CO ratio is high at 4:1. In Table 1 is listed the composition out from the reactor and the ratio between H_2 and CO decreases from almost 6:1 to 1:1 as residence time decreases. The CH_4 content in the gas decreases as residence time is decreased. This could be coupled with the cracking of tars as well as a possible methanation activity of the dolomite.

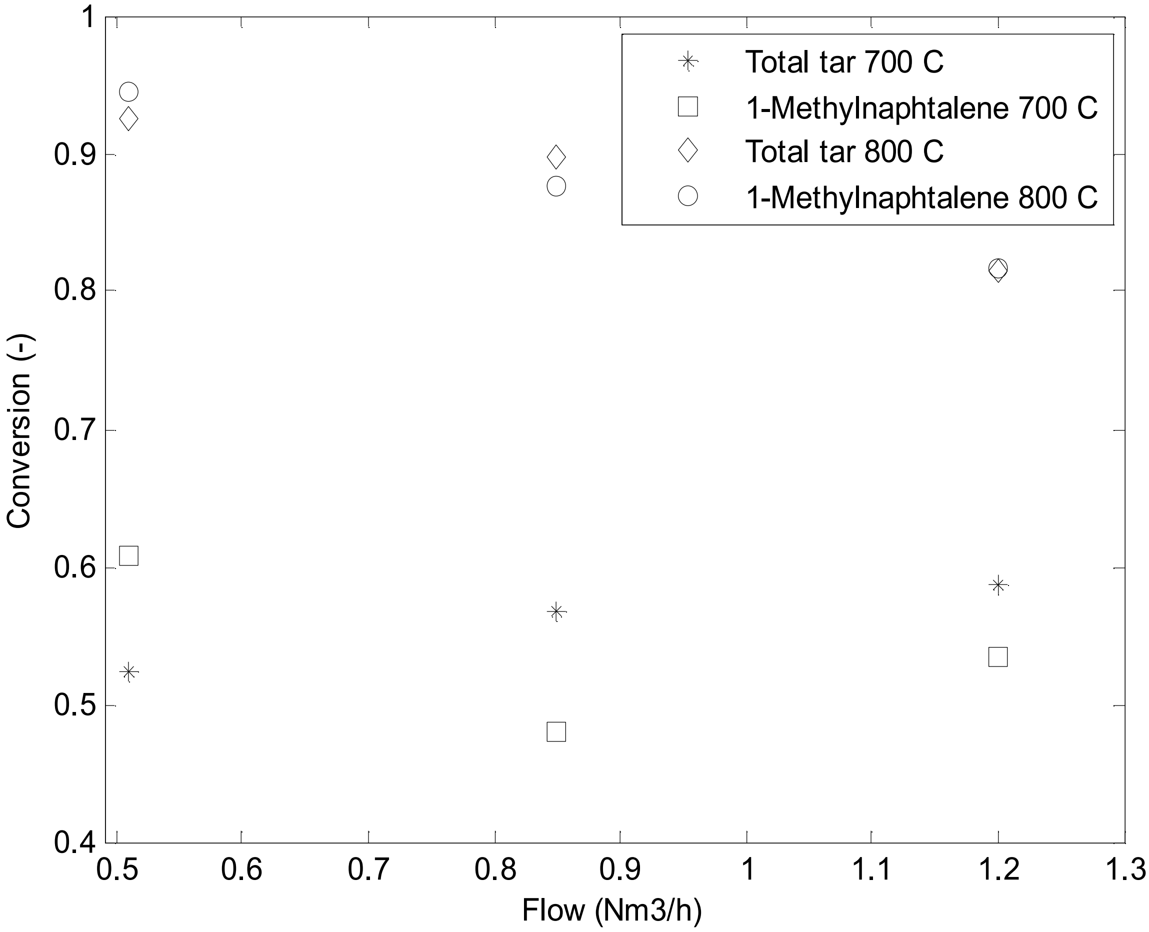

Figure 16 Tar conversion at different flow rates and temperatures.

As is seen in Figure 16, the conversion of the tar compound 1-methylnaphtalene is high with over 90 % for the lower flow rates. The total tar conversion, which includes BTX, is however lower at 50-60 % for all experiments. It should be noted here that the tar conversion is based on GC analysis and manual gas extraction. When looking at the flame it is very clear blue with mostly no visible white-yellow parts. It is very likely that a better tar analysis would have produced different values.

Figure 17: Series of images of flame at reactor outlet.

Figure 17 is a series of pictures of the flame at the reactor outlet described in Figure 7. The left most picture is when the gas is bypassed the reactor. The concentration of tars is 15,000 mg/Nm^3. The flame is very bright as can be seen when comparing the images to the right. There is no external lighting as that would make the rightmost flame almost invisible. The gas is then flowed through the reactor and the concentration of tars decrease rapidly. The gas flow is the same in all four pictures. The flames on the left with the high amount of tars in them are unstable, more like a candle flame, while the rightmost flame is more like a flame from a welding torch.

4.1.4 Ammonia cracking

The performance of the reverse flow reformer for ammonia cracking is shown in Figure 18. The inlet concentration is measured at around 1,400 vppm.

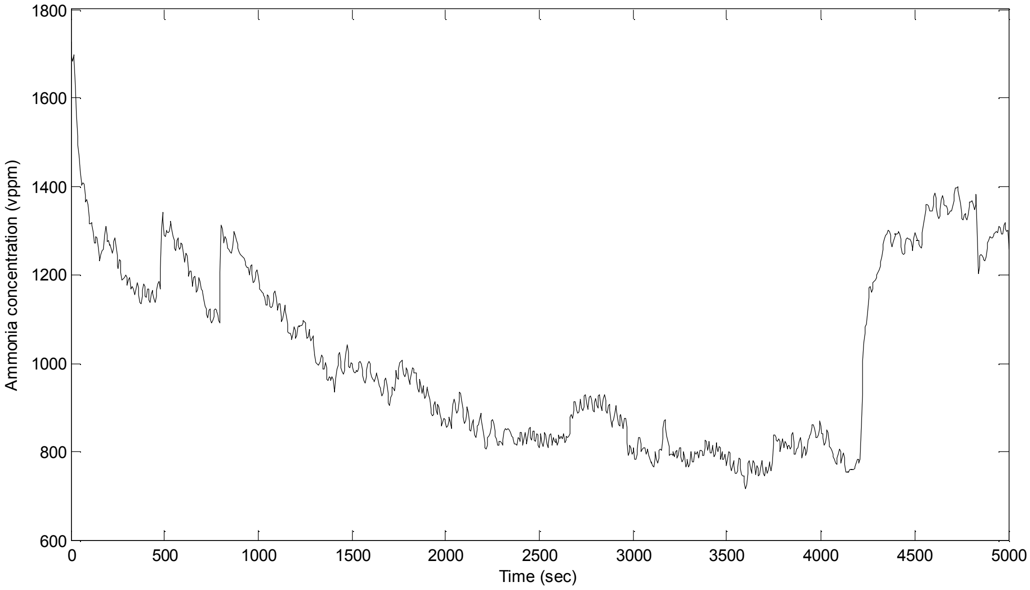

Figure 18 Ammonia concentration at the outlet of the reverse-flow reformer.

The ammonia cracking capabilities of the reverse-flow reformer on ammonia is not perfect under the studied conditions. It converts 40-50% of the ammonia in the gas. Residence time and GHSV were 15.3 seconds and 94 h^{-1} respectively. At the time around 4,250 seconds from the starting of measurement, the reactor is by-passed, allowing the measurement of the true input to the reactor.

4.1.5 Ammonia oxidation

Experimental runs of the selective oxidation of ammonia in synthesis gas over the catalyst can be seen in Figure 19.

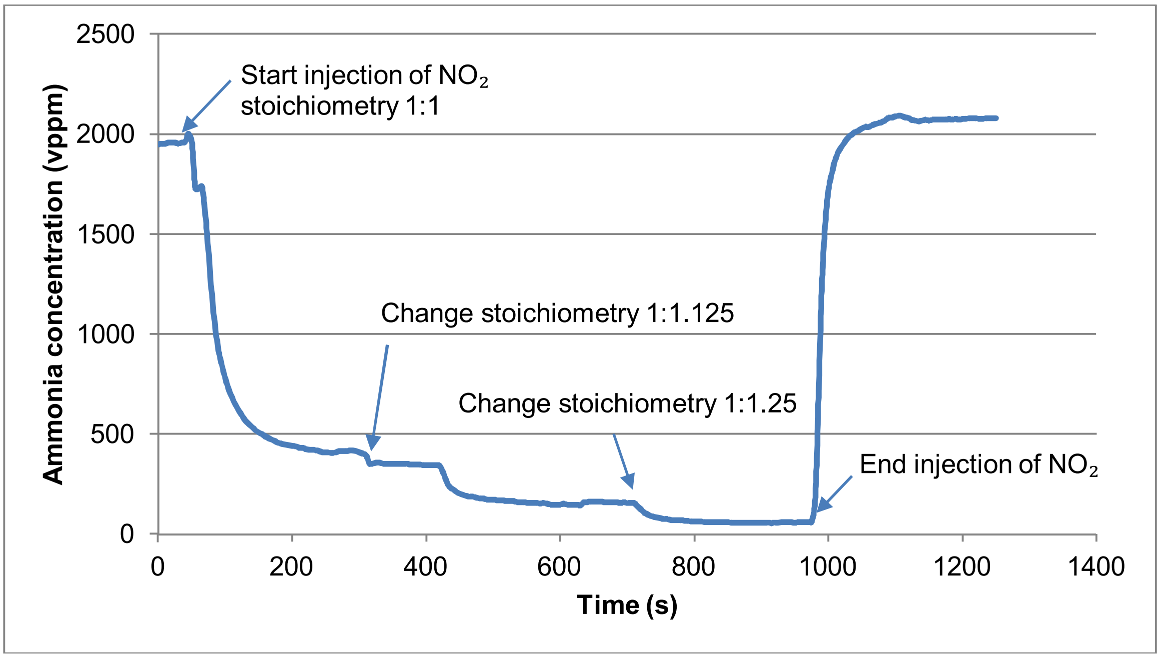

Figure 19 Ammonia concentration in outlet for $V_2O_5/WO_3/TiO_2$ at 325 °C.

Figure 19 shows a typical run for the ammonia oxidation system. Starting just below 2,000 vppm ammonia and after a few minutes the N_2/NO_2 is added to the stream. Initially the concentration of ammonia increases as the increased gas flow decreases the temperature over the catalyst. Thereafter the ammonia concentration drops rapidly to settle at around 340 ppm. The stoichiometry NO_2/NH_3 is increased to 1:1.125 and the outlet concentration falls to 150 ppm. The final stoichiomtery of 1:1.25 leaves the gas with only 50-60 ppm ammonia in the outlet. The N_2/NO_2 injection is then turned off and the ammonia concentration increases rapidly and settles around the starting concentration.

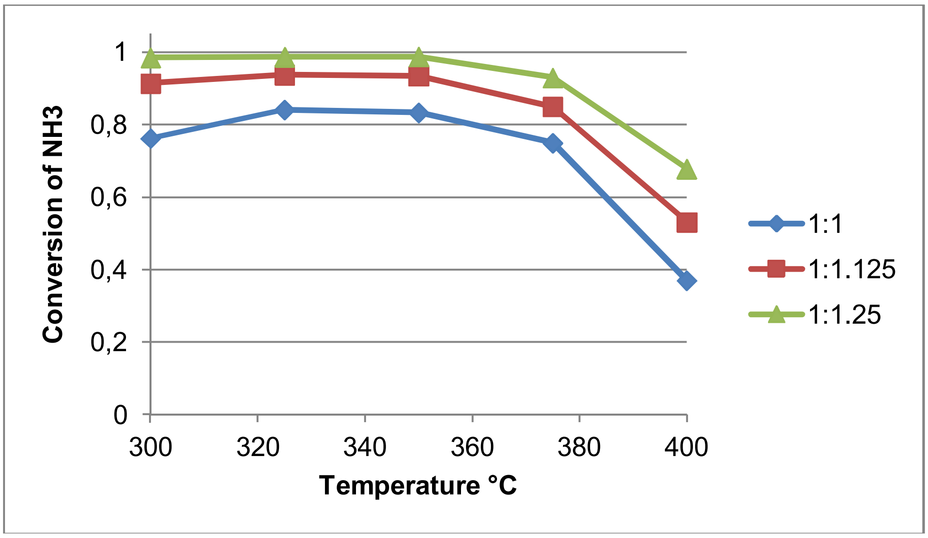

Figure 20 Conversion of ammonia at different temperatures for three NO_2/NH_3-stoichiometrics for the V_2O_5 based catalyst.

As seen in Figure 20 there is a very high conversion over the vanadium catalyst up to 350 °C after which it starts to decline. The total amount of NO_X, at the reactor outlet, was measured to roughly 50 ppm at 1:1, 50-100 ppm at 1:1.125 and slightly above 100 ppm at 1:1.25. NO_X-measurements were performed at 350 °C.

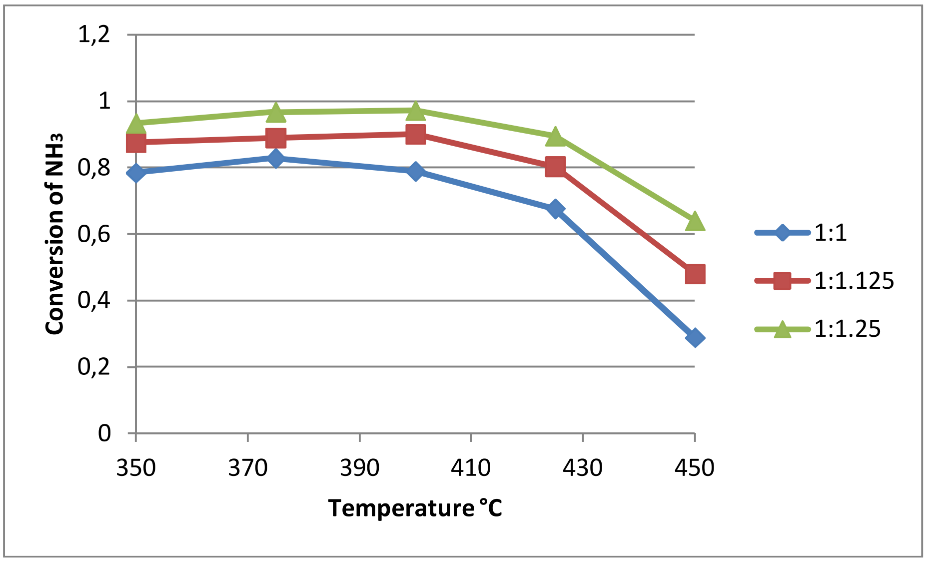

Figure 21 Conversion of ammonia at different temperatures for three NO_2/NH_3-stoichiometrics for the mordenite catalyst.

As depicted in Figure 21 the activity for mordenite is lower than for the vanadium based catalyst. The operating temperature is also higher with a peak in conversion at 400 °C for the two higher stoichiometrics. For 1:1 in stoichiometry the peak is at 375 °C. NO_X was measured at the reactor outlet to approximately 10 ppm at 1:1, 20 ppm at 1:1.125 and 90 ppm for 1:1.25 stoichiometry for 400 °C reactor temperature.

5 Conclusions

The reverse flow reformer performs rather well with respect to tar cracking, although it could have been a lot better, under the studied conditions. A part of the problem could be a result of the uncalcined packing material. The reactor was filled with uncalcined dolomite that was calcined during warm up of the reactor. This left parts of the reactor where the temperature was lower uncalcined which could affect both the tar reforming and ammonia cracking capabilities.

Methane content in the outlet was always above that of the inlet which is an indication that any tars cracked are converted into methane or that there is methanation activity on the dolomite surface. There are errors in the measurements, but not enough to put the methane content in the outlet below that of the inlet. With the tar cracking capabilities of the dolomite and the high methane content of the outlet, this results in a good tar cracker for SNG production or as a robust pre-reformer for other downstream synthesises.

The experimental reactor is over dimensioned for the lab, this is apparent when looking at the scaled up dimensions in Table 4. Since the total tar conversion increases with increased space velocity, under the studied conditions, it is not unrealistic to assume that increasing flow rates even further would at least not decrease the conversions while at the same time increase throughput. Pressures were atmospheric during the experiments, for ease of construction and safety. Higher pressures would also increase throughputs.

Ammonia conversion in the reverse flow pre-reformer was around 40-50% under the studied conditions. This puts the remaining ammonia in the gas at around 1,500 vppm for a producer gas with 3,000 vppm ammonia from the gasifier. With over 98% conversion in the selective ammonia oxidation reactor, this would result in around 10-30 vppm ammonia left. At these levels ammonia can safely be removed by condensed water prior to a compressor for downstream synthesis, or burned in a gas turbine or internal combustion engine without significant increases in nitrogen oxides in the exhaust. Future work should include tar cracking and ammonia reduction on a slip stream from a real gasifier using a real producer gas. There are a multitude of components present in real producer gas that cannot be duplicated in a model producer gas. Without all these components present, there is no possibility to evaluate the reverse flow reactor performance thoroughly. The same applies to the reverse SCR of ammonia. The problem that the reverse SCR may experience are all related to the catalysts ability to withstand the potential poisons in the gas such as sulphur, unconverted hydrocarbons from the reformer etc.

Future work would also include different bed material experiments, such as particle size and evaluation of different bed materials.

6 Literature

Albertazzi, S., Basile, F., Brandin, J., Einvall, J., Hulteberg, C., Fornasari, G., Rosetti, V., et al. (2005). The technical feasibility of biomass gasification for hydrogen production. *Catalysis Today*, *106*(1-4), 297–300. doi:10.1016/j.cattod.2005.07.160

Anis, S., & Zainal, Z. a. (2011). Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review. *Renewable and Sustainable Energy Reviews*, *15*(5), 2355–2377. doi:10.1016/j.rser.2011.02.018

Boreskov, G. K., & Matros, Y. S. (1983). Unsteady-State Performance of Heterogeneous Catalytic Reactions. *Catalysis Reviews*, *25*(4), 551–590. doi:10.1080/01614948308078056

Brandin, J. G. M., Andersson, L. A. H., & Odenbrand, C. U. I. (1989). Catalytic reduction of nitrogen oxides on mordenite some aspect on the mechanism. *Catalysis Today*, *4*(2), 187–203. doi:10.1016/0920-5861(89)85050-3

Devi, L., Ptasinski, K. J., Janssen, F. J. J. G., Van Paasen, S. V. B., Bergman, P. C. a., & Kiel, J. H. a. (2005). Catalytic decomposition of biomass tars: use of dolomite and untreated olivine. *Renewable Energy*, *30*(4), 565–587. doi:10.1016/j.renene.2004.07.014

Espenäs, B.-G., & Frostäng, S. (1999). *Catalytic Upgrading of Gas from Biofuels and Implementation of Electricity Production* (pp. 1–20). Termiska Processer AB Studsvik.

Evans, R. J., & Milne, T. A. (1997). Chemistry of Tar Formation and Maturation. In A. Bridgwater & D. Boocock (Eds.), *Developments in Thermochemical Biomass Conversion, vol 2* (pp. 803–816). London: Blackie Academic & Professional.

Fjellerup, J., Ahrenfeldt, J., Henriksen, U., & Gøbel, B. (2005). Formation, decomposition and cracking of biomass tars in gasification. Lyngby: Technical University of Denmark.

Han, J., & Kim, H. (2008). The reduction and control technology of tar during biomass gasification/pyrolysis: An overview. *Renewable and Sustainable Energy Reviews*, *12*(2), 397–416. doi:10.1016/j.rser.2006.07.015

Haynes, T. N., Georgakis, C., & Caram, H. S. (1992). The application of reverse flow reactors to endothermic reactions. *Chemical Engineering Science*, *47*(9-11), 2927–2932. doi:10.1016/0009-2509(92)87153-H

Held, J. (2012). *Gasification - Status and technology. SGC Rapport 240*. Malmö: Svenskt Gastekniskt Center.

Leppalahti, J. (1999). Process for removing ammonia from gasification gas. *US Patent 5,906,803*. United States Patent Office.

Matros, Y. S., & Bunimovich, G. A. (1995). Control of Volatile Organic Compounds by the Catalytic Reverse Process. *Industrial & Engineering Chemistry Research*, *34*(5), 1630–1640. doi:10.1021/ie00044a016

Matros, Y. S., & Bunimovich, G. A. (1996). Reverse-Flow Operation in Fixed Bed Catalytic Reactors. *Catalysis Reviews*, *38*(1), 1–68. doi:10.1080/01614949608006453

Milne, T. A., Abatzoglou, N., & Evans, R. J. (1998). Biomass gasifier“ tars”: their nature, formation, and conversion. Golden, CO: National Renewable Energy Laboratory. doi:10.2172/3726

Odenbrand, C. U. I., Gabrielsson, P. L. T., Brandin, J. G. M., & Andersson, L. A. H. (1991). Effect of water vapor on the selectivity in the reduction of nitric oxide with ammonia over vanadia supported on silica-titania. *Applied Catalysis*, *78*(1), 109–122. doi:10.1016/0166-9834(91)80092-B

Rabou, L. P. L. M., Zwart, R. W. R., Vreugdenhil, B. J., & Bos, L. (2009). Tar in Biomass Producer Gas, the Energy research Centre of The Netherlands (ECN) Experience: An Enduring Challenge. *Energy & Fuels*, *23*(12), 6189–6198. doi:10.1021/ef9007032

Svensson, H., Tunå, P., Hulteberg, C., & Brandin, J. (2012). Modeling of soot formation during partial oxidation of producer gas. *Fuel*, (In press). doi:10.1016/j.fuel.2012.10.061

Torres, W., Pansare, S. S., & Goodwin, J. G. (2007). Hot Gas Removal of Tars, Ammonia, and Hydrogen Sulfide from Biomass Gasification Gas. *Catalysis Reviews*, *49*(4), 407–456. doi:10.1080/01614940701375134

Tunå, P., & Brandin, J. (2013). Selective catalytic oxidation of ammonia by nitrogen oxides in a model synthesis gas. *Fuel*, *105*, 331–337. doi:10.1016/j.fuel.2012.08.025

Tunå, P., Svensson, H., & Brandin, J. (2010). Modeling of Reverse Flow Partial Oxidation Process for Gasifier Product Gas Upgrading. *Fifth International Conference on Thermal Engineering: Theory and Applications*. Marrakesh.

Van de Beld, L., Wagenaar, B. M., & Prins, W. (1997). Cleaning of hot producer gas in a catalytic adiabatic packed bed reactor with periodic flow reversal. In A. V. Bridgwater & D. G. B. Boocock (Eds.), *Developments in Thermochemical Biomass Conversion, vol 2* (pp. 907–920). London: Blackie Academic & Professional.

Xu, C., Donald, J., Byambajav, E., & Ohtsuka, Y. (2010). Recent advances in catalysts for hot-gas removal of tar and NH3 from biomass gasification. *Fuel*, *89*(8), 1784–1795. doi:10.1016/j.fuel.2010.02.014

Zhou, J., Masutani, S. M., Ishimura, D. M., Turn, S. Q., & Kinoshita, C. M. (2000). Release of Fuel-Bound Nitrogen during Biomass Gasification. *Industrial & Engineering Chemistry Research*, *39*(3), 626–634. doi:10.1021/ie980318o