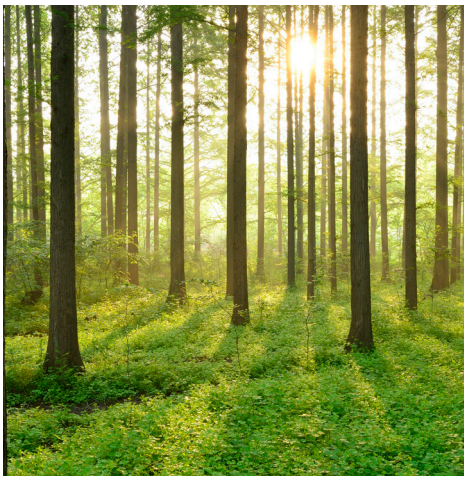
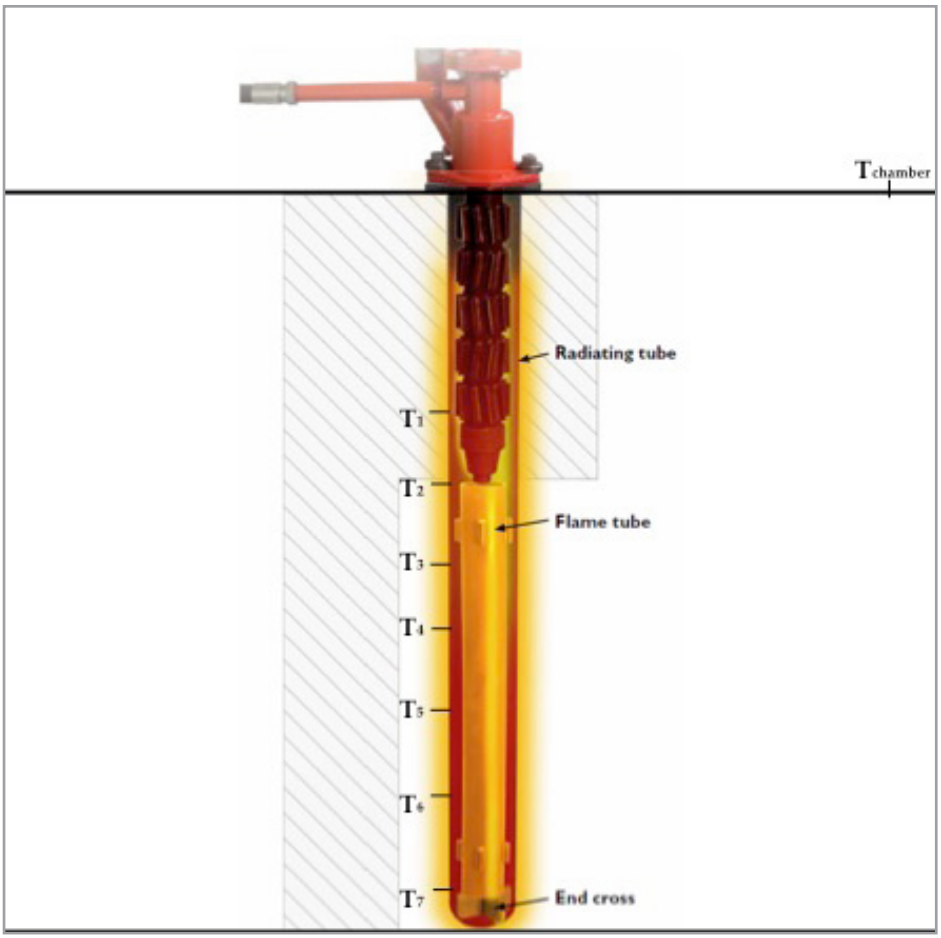
CATALYTIC CONVERSION OF PYROLYSIS GAS IN THE WOODROLL® PROCESS

REPORT 2016:340



ENERGY GAS TECHNOLOGY



Energiforsk

Catalytic Conversion of Pyrolysis Gas in the Woodroll® Process

For Enhanced Process Reliability

POUYA HAGHIGHI MOUD
DENNIS FÄLLÉN HOLM
ALFRED HALVARSSON
KLAS ANDERSSON
EFTHYMIOS KANTARELIS
MARKO AMOVIC
ROLF LJUNGGREN
KLAS ENGVALL

ISBN 978-91-7673-340-0 | © 2016 ENERGIFORSK

Energiforsk AB | Phone: 08-677 25 30 | E-mail: kontakt@energiforsk.se | www.energiforsk.se

Foreword

This project evaluated a novel technology for gasification of biomass to be implemented in the production of alternative fuels, renewable energy gas and chemicals. The biggest challenge for the commercialization of the WoodRoll® process is the integration of all the process steps in a continuous process.

The report has been produced by KTH, Cortus Energy AB and Haldor Topsoe A/S and the authors are Pouya Haghighi Moud, Dennis Fällén Holm, Alfred Halvarsson, Klas J. Andersson, Efthymios Kantarelis, Marko Amovic, Rolf Ljunggren and Klas Engvall.

The study was funded by the Swedish Energy Agency, through the Swedish Energy Research Centre and the Co-operation Program Energy gas technology, Cortus Energy AB and Haldor Topsoe A/S. The study had a reference/working group with the following members: Anton Fagerström (Energiforsk), Klas Engvall (KTH), Rolf Ljunggren (Cortus Energy AB), Klas J Andersson (Haldor Topsoe A/S).

Sammanfattning

Utvecklingen av ett hållbart biobaserat samhälle kräver utveckling av förnybara energiprodukter och kemikalier. En viktig bas i ett integrerat system för förnybar produktion av alternativa drivmedel, energigas och kemikalier är biomassa. Biomassa kan bland annat konverteras genom termokemisk omvandling, t.ex. förbränning, förgasning, pyrolys eller förvätskning, kan ingå sådana integrerade system. Pyrolys och förgasning är två intressanta alternativ, men har i dagsläget svårt att på ett kostnadseffektivt sätt producera produkter i konkurrens med produkter baserade på fossil råvara. För att uppnå en högre grad av kommersialisering och då framförallt för anläggningar i mindre till medelstor skala krävs utveckling av bättre och effektivare processtekniska lösningar.

Cortus Energy AB har utvecklat en patenterad förgasningsteknologi, WoodRoll®, för förgasning av biomassa där processen är uppdelad i tre steg – torkning, pyrolys och förgasning. Den största utmaningen för en kommersialisering av WoodRoll®-processen är integrationen av alla delarna i en kontinuerlig process. Hanteringen av den gas, som produceras vid pyrolysen och innehåller en stor andel tyngre kolväten i form av olja eller tjära, är här en viktig del utvecklingen. Problem som behöver adresseras är möjlig kondensering av tjära eller pyrolysolja i rörledningar och ventiler mellan pyrolysreaktor och brännare i förgasningsreaktorn samt att uppnå en jämn förbränning av pyrolysgasen i strålningstubbrännarna. Att reducera de höga installationskostnader för instrumentering för höga temperaturer samt varmhållning av ett komplett rörsystem, som används idag, är en annan drivkraft. Genom omvandling av pyrolysgasen sänks kondensationstemperaturen. Med lägre temperaturer i brännarsystemet ges en möjlighet till sänkta kostnader, vilket är grunden för att utreda detta alternativ.

Projektet har tittat på möjligheten att utnyttja direkt katalytisk reformering av pyrolysoljan i pyrolysgasen till lättare oljor med lägre kondensationstemperatur eller lättare gasmolekyler. Målet är för att uppnå en ökad processtabilitet och flexibilitet. Sammanfattningsvis så pekar resultaten på stora möjligheter att använda tekniken i WoodRoll®-processen. Processer för katalytisk omvandling av biomassa-baserad pyrolysolja under utveckling kräver generellt omfattande rening av bl.a. svavel för att undvika deaktivering. Katalytisk omvandling kunde dock utföras med bibehållen katalytisk aktivitet under upp till 8 timmars exponering för en verklig oljerik pyrolys gas med endast partikelfiltrering före katalysatorn. En reducering av mängden pyrolysolja på ca 57 % kunde uppnås vid försöken. Samtidigt ökade gasvolymen väsentligt efter omvandlingen. Även pyrolysoljans sammansättning förändrades där andelen syreinnehållande kolväten minskade efter omvandlingen. Förbränningen av gasen i brännaren visade på ett förändrat uppträdande där bl. a. halterna av NO/NOx var lägre för den omvandlade gasen jämfört med den råa pyrolysgasen. Förbränningen startade även närmare

brännarens munstycke, vilket innebär en snabbare förbränning och jämnare flamma.

Resultaten pekar även på att tekniken kan komma att bli ett av stegen i en process för produktion av gas av syntegaskvalité, direkt från oljerika pyrolysgaser. Detta öppnar upp för en generell användning av tekniken i pyrolysprocesser. Tekniken visar även på möjligheten att utvecklas till en process för reduktion av syreinnehållande oljeföreningar i pyrolysolja, vilka är ett stort problem vid lagring av pyrolysolja, då dessa föreningar ofta polymeriserar till tjocka svårpumpade oljor.

Summary

The advancement of a sustainable bio-based society requires development of renewable energy products and chemicals. An important platform in an integrated system for renewable production of alternative fuels, energy gas and chemicals is biomass. Biomass may be converted by thermochemical conversion, e.g. combustion, gasification, pyrolysis or liquefaction, which are possible options in integrated systems. Pyrolysis and gasification are two interesting alternatives, but in the current situation is it difficult to in a cost-efficient way produce products in competition with products, based on fossil raw materials. To achieve a higher degree of commercialization and especially for installations in small to medium scale, the development of better and more efficient engineering solutions is required.

Cortus Energy AB has developed a patented gasification technology, WoodRoll®, biomass gasification, where the process is divided into three steps - drying, pyrolysis and gasification. The biggest challenge for the commercialization of the WoodRoll® process is the integration of all the process steps in a continuous process. The handling of the gas, produced during pyrolysis, including a large fraction of heavier hydrocarbons in the form of oil or tar, is an important part of development challenge. Problems that need to be addressed are possible condensation of tar or pyrolysis oil in the pipeline and valves between the pyrolysis reactor and burners in the gasification reactor, and to achieve a uniform combustion of the pyrolysis gas in the burners. Reduction of the large installation costs for high temperature instrumentation used today, as well as for trace heating of a complete piping system is another driving force. By converting the pyrolysis gas the condensation temperature is lowered. Lower temperatures in the burner system facilitate lower equipment costs, which is the basis for evaluating this alternative.

The project has considered the possibility utilizing direct catalytic reforming of the pyrolysis oil in the pyrolysis gas into lighter oils with lower condensation temperature or to gas molecules. The goal is to achieve an improved process stability and flexibility. In summary, the results indicate a great potential to apply the studied technology in the WoodRoll® process. Processes for catalytic conversion of biomass-based pyrolysis under development, requires generally, extensive purification to avoid e.g. sulphur deactivation. Catalytic conversion could, however, be carried out maintaining the catalytic activity for up to 8 hours of exposure to a real oil-rich pyrolysis gas, with only particulate filtration prior to the catalyst. A 57 % reduction in the amount of pyrolysis oil could be achieved in the tests. At the same time the volume of gas increased significantly after the conversion. Even the composition of the pyrolysis oil changed where the proportion of oxygen-containing hydrocarbons decreased after the conversion. The combustion of the gas in the burner displayed a changed behaviour which, for example, the levels of NO/NOx was lower for the converted gas, compared to the

crude pyrolysis oil. The burning started even closer to the burner nozzle, which means a more rapid combustion and a more uniform flame.

The results also show that the technology may be used as one of the steps in a process to produce of gas of syngas quality, directly from the oil-rich pyrolysis gases, which also opens up for a general use of the technology in pyrolysis processes. It is also shown that it may be possible to develop the technology to a process for reduction of the oxygen-containing compounds in pyrolysis oils. These compounds are major obstacle in storage of pyrolysis oils, as they often polymerize into thick oils difficult to pump.

List of content

1 Introduction

The development of a sustainable bio-based society requires a development of renewable energy products and chemicals. Biomass is an important platform in an integrated system for renewable production of alternative fuels, energy gas and chemicals. Biomass may be converted by thermochemical conversion, e.g. combustion, gasification, pyrolysis or liquefaction, where gasification and pyrolysis are interesting options to produce intermediate energy carriers in form of pyrolysis oil and product gas. Intermediates that can be used directly of further upgraded in such integrated systems. Nevertheless, products form pyrolysis and gasification of biomass is today not cost efficient enough to compete with similar products, based on fossil raw materials and therefore technologies for this purpose have lower degree of commercialization than desired. To achieve a higher degree of commercialization, especially for installations in small to medium scale, a development of better and more efficient engineering solutions is needed.

Cortus Energy AB has developed a patented technology, WoodRoll®, for biomass gasification [1, 2]. The process is divided into three stages - drying, pyrolysis and gasification. In the pyrolysis stage, carried out at 380-420 °C, charcoal and pyrolysis gas is formed. The charcoal is transported up to the gasifier, where it is indirectly gasified at temperature of about 1100 ° C together with steam. Heat for the gasification process is obtained by combustion of the pyrolysis gas in radiant heat burners, placed in the gasification reactor. The pyrolysis gas is a complex mixture, consisting of permanent gases, pyrolytic biomass, minor amounts of ash components and pyrolysis oil. The latter is a complex mixture of organic compounds and consists of a large proportion of oxygenated organic compounds e.g. acids, alcohols, aldehydes, ketones, substituted phenols, and oxygenates from the lignin complex. The burners in the process should be operationally reliable, have a long operating lifetime and should practically completely combust all components in the pyrolysis gas, except solid components separated in a filter before the burners. Today there is no guarantee that the burners meet these requirements. Another challenge is a possible condensation of the pyrolysis oil vapour in the gas at temperatures lower than the temperature used in the pyrolysis. This means that the gas pipelines conveying the gas to the burners must maintain a temperature at least equal to that used in the pyrolysis stage. Cold spots inevitably lead to condensation and most likely to clogged pipes. A process, such as a catalytic conversion process, reducing the amount of condensable pyrolysis oil and/or converting the heavier oil fractions to lighter is therefore desirable to decrease the problems.

1.1 AIM AND SCOPE

The scope of the project was to perform an early evaluation of a technical solution, based on a catalytic conversion, simplifying the conveying of the pyrolysis gas in pipelines and valves as well as improve combustion properties in the radiant heat tube burners. The evaluated technology may at a later stage also be furher developed into a process step included in a production system for clean energy gas, or syngas, which provides additional process advantages. The internal energy

supply in the WoodRoll® process could then be diversified, enabling, for example, storage of the gas and use when required. Furthermore, energy gas could then be delivered even during downtime in the gasifier.

2 Background and Theory

2.1 PYROLYSIS OF BIOMASS

Ligno-cellulosic biomass is complicated in structure and in composition and differs also radically from fossil feedstocks [3]. The main components in ligno-cellulosic biomass are the polysaccharides cellulose and different types of hemi-celluloses and pectins, the complex aromatic polymer lignin, organic extractives and inorganic minerals. All organic compounds in lignocelluloses contain oxygen, but the degree of oxidation varies, so that the polysaccharides contain more oxygen than lignin and the extractives. Cellulose, hemi-cellulose and lignin are oxygen-containing carbohydrates and the quantities vary between different types of biomass plants. Each of these components has their own pyrolysis chemistry in thermo-chemical conversion, and therefore the composition of the volatilised intermediary compounds can vary substantially depending on biomass used.

Pyrolysis is a highly adaptable endothermic thermochemical decomposition process where the complex macromolecules of biomass is converted into permanent gas, vapour and solid [4] in absence of an oxidizing agent, according to the reaction:

Feedstock → char + vapours + CO_2 + H_2O + CH_4 + CO + H_2 + (C_2 – C_5) + impurities (1)

The quality and relative proportion of the products, permanent gas, char and pyrolysis oil, depend on several factors such as temperature, heating rate, vapours residence time, pressure, biomass composition, etc. Pyrolysis generally starts at 300 °C and continues up to 600–700 °C – those limits are not absolute – leading to the formation of the abovementioned products. Generally, lower process temperature and long vapour residence time favour char production, whereas high temperature and long vapour residence time increase the gas yield. Moderate temperature and short vapor residence time favor production of liquids. [5]

Temperature ranges and residence times for slow, intermediate and fast, as well as a few other examples of pyrolysis processes are presented in Table 1.

Table 1 Temperature ranges and heating rates for slow, intermediate and fast pyrolysis as well as examples of other pyrolysis processes. Adapted from Tripathi et al and Yang et al [6, 7]

	Slow	Intermediate	Fast	Hydro pyrolysis	Flash
Temperature [°C]	550-950	500-650	850-1250	350-600	900-1200
Heating rate [°C/s]	0.1-1.0	1.0-10	10-200	10-300	>1000

In case of the WoodRoll® technology pyrolysis process, the temperature and heating rate is around 350-400 °C and 1-2 °C/s, respectively, implying a hybrid pyrolysis process.

The vapours are known as bio-oil, bio-crude or pyrolysis oil, and are a complex mixture of mainly oxygenates, aromatics, water, products of low degree of polymerization and tars. The hydrocarbon fraction of the pyrolysis may also be

classified according to: hydroxyaldehydes, hydroxyketones, sugars and dehydrosugars, carboxylic acids, and phenolic compounds [8].

Highly oxygenated pyrolysis oil may signify a number of negative aspects, compared to deoxygenated oil. The problems may both influence the process equipment during operation as well as the product formed. The pyrolysis oil vapours readily form deposits on solid materials as a result of the carbonaceous coke formation during tar-cracking and the condensation of oil on cold surfaces, causing possible problems with clogging [9].

Oxygen rich oil has also a higher viscosity and is also more corrosive than oil with low oxygen content. Part of the oxygenated compounds is also unstable and prone to react and polymerize to larger molecules [10], forming fractions with even higher viscosity in the end resulting in separation of the oil in different viscous phases. This is a problem when storage of the pyrolysis oil is desired.

2.2 CONVERSION OF PYROLYSIS OIL

Catalytic conversion of pyrolysis oil equivalent in a temperature range equal to a low temperature pyrolysis process is either similar to adiabatic pre-reforming of C_1 - C_5 hydrocarbons, naphtha, gas oil, simple aromatics, and diesel, a part of the well established industrial steam reforming process for synthesis gas production [11], or to hydrodeoxygenation (HDO) for producing a gasoline like product [12]. The two types of processes are briefly described below.

2.2.1 Adiabatic pre-reforming

Catalytic adiabatic pre-reforming converts various hydrocarbons by steam reforming at low temperature, 350 to 550 ° C, directly to methane and carbon monoxide without any intermediate products [13]. In steam reforming hydrocarbons react with steam at high temperatures, 300-800 °C, converting the hydrocarbons to CO and H_2, as shown in reaction (2). Steam reforming is normally accompanied by the water gas shift (WGS) and the methanation reaction, displayed in reactions (3) and (4). The extents of these reactions depend on the operating conditions. [11, 14, 15]

Steam reforming: $C_xH_y + xH_2O \leftrightarrows xCO + (x + y/2)H_2$ (2)

WGS: $CO + H_2O \leftrightarrows CO_2 + H_2$ (3)

Methanation: $CO + 3H_2 \leftrightarrows CH_4 + H_2O$ (4)

The reforming reaction is an endothermic reaction and favoured by high temperatures and low pressures. The reactions methanation and WGS are exothermic, where the WGS is shifted toward CO and H_2O at high temperatures. In case of bio-based pyrolysis oils rich in oxygenates, the general reaction scheme for steam reforming is:

$$CxHyOz + (x - z)H_2O \rightarrow xCO + (x - z + y/2)H_2 \quad (5)$$

In combination with WGS this reaction can be transformed to:

$$C_xH_yO_z + (2x - z)H_2O \rightarrow xCO + (2x - z + y/2)H_2 \quad (6)$$

Steam reforming of oxygenates is generally described by (6) but in case of high temperatures WGS (3) is shifted to the left and the CO is then increased. Also, the methanation in reaction (4) influence the product distribution, especially at low temperatures [14]. Important to note is that the reactions in (5) and (6) are for complete conversion to synthesis gas.

In an industrial steam reforming process, the pre-reforming step is generally included to allow for feedstock flexibility and a higher inlet temperature to the main reformer, since higher hydrocarbons are converted to CH_4, before they reach zones with high temperatures where they otherwise may cause carbon deposition by whisker formation at high temperatures [16].

The traditional common catalyst material used in the industrial fossil fuel steam reforming is Ni [15]. In model studies using acetic acid, Ni has also been proven to be a superior candidate, in comparison with other investigated metallic materials such as Co, Fe and, Cu [17]. In this particular case, Co and Ni can achieve complete conversion at 450 °C and a LHSV of 8.3 h^{-1}, while Fe and Cu achieved roughly around 25 % [18]

Besides metallic catalysts, also simpler cheaper mineral-based materials, such as calcite and dolomite, have been suggested as a catalyst for a [17, 19]. The lime-based material is not as active as metallic catalysts, but the materials has to a greet degree been investigated for their tar-cracking ability [20]. It is a widely spread naturally occurring rock mineral with the chemical formula $CaMg(CO_3)_2$ having a distribution of approximately 1:1 of Ca:Mg [21]. The major benefits with dolomite are its high activity toward cracking oil and the plentiful supply of the mineral making it a low- cost alternative. A drawback is that high activity generally are obtained at elevated temperatures above 800 °C [20].

2.2.2 Hydrodeoxygenation (HDO)

Hydrodeoxygenation is a hydrolytic cleavage of a carbon and oxygen bond that removes oxygen and consequently decreasing the sizes of the molecules in the oil. The reduced oxygen content in the oil also increases the stability A HDO treated oil has also a higher heating value than the original crude oxygenated pyrolysis oil. [22]

There are several reactions proposed for the removal of oxygen from the oil, viz., dehydration, decarboxylation and decarbonylation. Literature covering HDO on biomass pyrolysis oil is largely composed of studies conducted on model compounds, such as guaiacol or anisole [23, 24], or mixtures of simple aromatic compounds [22]. Further evaluation on how large molecules from pyrolysis of lignin-based biomass influence the process is therefore needed. A generalized mechanism is proposed by Dayton [25] as shown in reactions (7) and (8).

$$C_5H_8O_4 + 6H_2 \rightarrow 6CH_2 + H_2O \quad (7)$$

$$C_5H_8O_4 + 4.5H_2 \rightarrow 6CH_{1.5} + 4H_2O \quad (8)$$

However, in reality the processing of a pyrolysis oil is much more complex, due to the large number of different oxygenated compounds in the oil, and the mechanisms are thus far from understood.

Hydrodeoxygenation (HDO) can be performed either in liquid or vapour phase, where liquid phase HDO is most thoroughly examined. The liquid process is performed with heterogeneous catalysts in the presence of hydrogen at temperatures of 200-300 °C at a pressure around of 50 bar [23, 26]. In comparison to liquid phase HDO, the process conditions for vapour phase HDO are completely different, where a vapour of the oil, generally at ambient pressure and temperatures above 400 °C, is fed into reactor [24]. A temperature above 400 °C is used to minimize condensation of the oil components. An advantage of using a vapour phase HDO system, as proposed in the present study, is the avoidance of heat losses since there is no need to condensate the pyrolysis oil prior to the HDO process, compared to the liquid phase HDO process. Several different types of catalysts adhering to different chemical species or classes have been used to promote the HDO reaction. These types of catalysts include carbides, noble metals, reducible metal oxides, nickel molybdenum (Ni-Mo) and cobalt molybdenum (Co-Mo) catalysts, as well as low cost base metals [27, 28].

2.2.3 Other reactions

Beside steam reforming and HDO other possible reactions may be active in converting the pyrolysis oil. Examples of relevant reactions are decarbonylation, decarboxylation and dehydration [29] as exemplified in reactions (9), (10) and (11), respectively.

$$R\text{-}CHO \rightarrow R\text{-}H + CO \quad (9)$$

$$R\text{-}CH_2\text{-}COOH \rightarrow R{=}CH + CO_2 + H_2 \quad (10)$$

$$R\text{-}CH_2\text{-}OH \rightarrow R{=}CH + H_2O \quad (11)$$

$$R\text{-}CH_2\text{-}COOH \rightarrow R{=}CH + CO + H_2O \quad (12)$$

2.2.4 Catalyst deactivation

Carbon formation on the catalyst surface is the main limiting factor in selecting operating conditions. The water content in the gas prevents carbon formation and therefore is the steam-to-carbon ratio particularly important. The largest problem in case of Ni-based catalysts is the sulphur in the feedstock. Sulphur reacts readily with the catalytically active Ni and form non-active NiS [13]. How much sulphur that may be tied in the catalytic reactor is controlled by factors such as catalyst materials, temperature, S and H_2 content in the gas phase. Hydrogen in the gas pushes the equilibrium towards the formation of H_2S and reduces the probability of metal sulphide formation. The S content in the biomass is relatively low, 0.01 to 0.2 %, compared to e.g. fossil raw materials such as naphtha, 1.5% [29]. Amount of sulphur released into the gas phase of remaining in the char, after pyrolysis is controlled by, for instance, the pyrolysis temperature.

Furminsky and Massoth [30] stated the main factor governing the lifetime of the catalyst is the loss of active sites via deactivation, where the deactivation by sintering, pore constriction, coking and poisoning by e.g. S is related to the active and support material selected.

2.3 THE WOODROLL® PROCESS

The WoodRoll® gasification process is divided into three main steps: drying, pyrolysis and gasification [2]. A separation of the processes enables production of a syngas with reduced content of impurities and condensable heavy fractions as well as minimizes the nitrogen dilution. As the process is divided in stages a higher degree of fuel flexibility is possible as mixing and purification can be handled in the most efficient stage of operation. Biomass flexibility is the cornerstone for the WoodRoll® technology. Wet and bulky to dry and dense materials can be used according to tests performed. Biomass is normally supplied to the plant by truck. This incoming material, preferably at loading switches containers, is received and weighed in a reception center to be filled in large pockets. The different stages are illustrated in Figure 1 and briefly outlined in forthcoming subsections below.

2.3.1 Drying

Drying of biofuel is the first stage of the process. The dryer is indirectly heated in a rotary drum with heat exchanging tubes. The particular process is well proven for a variety of materials with proper control of heating and mixing in the reactor. A hot gas reactor is supplying the heat by burning pyrolysis gas from subsequent steps. Dried fuel is then transferred to a pyrolysis reactor.

2.3.2 Pyrolysis

Dried fuel is airtight transferred to a pyrolysis reactor. The reactor is similar to the dryer but runs at much higher temperature for heating and homogenization of the produced char. Heat is mainly generated from the flue gas from the gasification stage downstream. Pyrolysis gas is generated with condensable pyrolysis oil also called tar in gas phase. The produced gas is conveyed to the burners supplying the heat to the gasification process in the gasifier. The reactor is gas tight and runs at a slight overpressure. Airlocks in incoming biofuel and outgoing char are handled properly. Char is cooled and grinded to required size before entering the gasifier.

2.3.3 Gasification

The gasifier is designed for entrained gasification of char and steam. Radiant tube heat burners supply the heat where the pyrolysis gas, consisting of both gaseous and condensable (liquid) products, is combusted.

Char and steam are injected to the gasifier. Superheated steam is mixed with char as well as the atmosphere in the gasifier for optimum reaction conditions. Ash (salts and minerals) is preferably separated in a cyclone before entering the syngas cooler/heat exchangers.

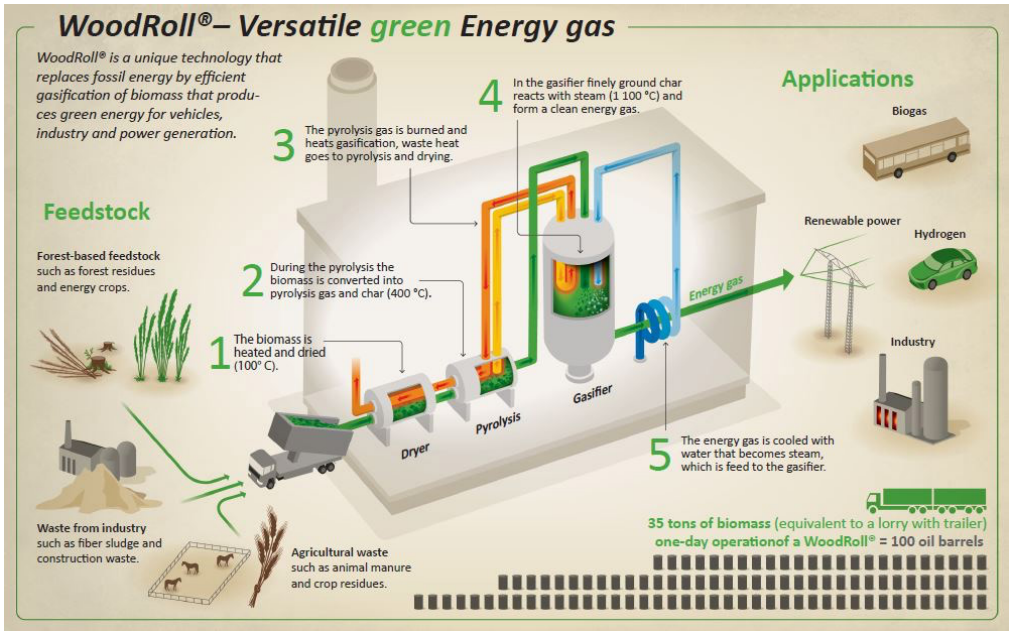


Figure 1 Illustration of the WoodRoll® gasification process

The crude product gas produced in the WoodRoll® process has typically a gas composition consisting of 16-20 % CO, 20-24 % CO_2, 55-65 % H_2, 2-3 % methane, minor amount of higher hydrocarbons in form of benzene as well as impurities, such as ammonia, HCN, and H_2S. The amounts of impurities are relatively low compared to other gasification technologies.

3 Experimental

For practical reason, the experimental work was divided in two parts where the first part was performed in the laboratories at KTH and the second at Cortus test site in Köping. The tests at KTH enabled investigation and selection of test equipment, materials and methods for sampling and chemical analysis most suitable for the large scale in Köping. The following sections provide an overall description of all methods and equipment used in the experimental work

3.1 MATERIALS

3.1.1 Catalysts

Primarily two types of catalysts were used in the tests an iron-based and a dolomite-based catalyst.

Iron-based catalyst (HT-25934): The Fe-based catalyst provided by Haldor Topsoe needs to be activated in a reducing gas. Activation may be carried out by exposure to CO and H_2 in the pyrolysis vapour in the initial use of the catalyst, as further described in Section 3.3.2.

Dolomite: Dolomite is a mineral and a dolomite rock consists of more than 90 % of the mineral dolomite ($MgCa(CO_3)_2$) and less than 10 % of the mineral calcite. Most dolomite is associated and often interbedded with limestone [31]. The dolomite used in the present study was from Sala Mineral AB. In order to be active also the dolomite need to be activated. This is carried out by precalcination of the material at elevated temperature prior to loading the catalyst into the catalytic reactor, according to reaction (12) and (13).

$$CaMg(CO_3)_2(s) \rightarrow CaO(s) + MgO(s) + 2CO_2(g) \quad (13)$$

$$CaMg(CO_3)_2(s) \rightarrow CaCO_3(s) + MgO(s) + CO_2(g) \rightarrow MgO(s) + CaO\,(s) + 2CO_2(s) \quad (14)$$

The general view is that dolomite decomposes in a single step (13) and in two steps (14) at low (< 26.7 kPa) and high (> 26.7 kPa) partial pressure of CO_2, respectively [32]. In the two steps decomposition process, the double carbonate is first decomposed to MgO at a temperature of 780 – 800 C and $CaCO_3$, and thereafter the $CaCO_3$ is decomposed to CaO in the second step at temperature of 880 – 900 °C. The single step reaction generally takes place at a temperature around 700 °C.

The dolomite pellets were calcined batch-wise in batches of 250 ml in a Carbolite CWF 1200 lab- oratory chamber furnace. The batches were prepared by applying a single layer of dolomite on a ceramic tray. This was done to counteract incomplete calcination attributed to a build-up of thermal gradients within the sample, where the thermal gradients had proved to have a negative effect on the curing, i.e. causing concentration gradients of CO_2 within the sample, thus yielding a mineral that was not cured homogeneously.

The first batch was calcined for two hours at a temperature of 900 °C with a temperature ramping rate of 5 °C/min. Visual inspection indicated that the

curing was not complete as white and partially white pellets were observed in the otherwise brownish catalyst sample. The second batch was therefore calcined for three more hours under the same operation conditions as presented above. The remaining batches were calcined for 5 hours at the same temperature and ramping rate making up a total catalyst volume of 2 l.

3.1.2 Biomass feedstock used

In the tests at KTH, birch chips of a size of 1-3 mm were used as a feedstock. The tests at Cortus facility in Köping were carried out using chips of tree-tops and branches "GROT". The properties and composition of the two biomasses are shown Table 2 and Table 3.

Table 2 Ash and moisture content of birch and GROT biomass

Proximate analysis	Birch	GROT
Ash, 550 °C	0.40 % dry basis	1.6 % dry basis
Moisture, 105 °C	6.5 %	30-55 %

Table 3 Composition of birch biomass, ultimate analysis

Ultimate analysis (wt-% dry basis)	Birch	GROT
C	49.0	50.4
H	6.0	6.0
O	44.4	41.6
N	0.18	0.43
Cl	0.01	<0.02
S	<0.012	0.03

3.2 EXPERIMENTAL SET-UPS

3.2.1 Set-up at KTH

The tests at KTH were performed to both evaluate a newly constructed setup with three bench-scale size reactors, but also to assess operational conditions and methodologies for characterizing and chemical analysis of samples collected. Figure 2 shows a schematic block diagram of the experimental setup, consisting of a pyrolyser, a high temperature filter, the setup with three catalytic reactors and the gas analysis and pyrolysis oil sampling blocks. The different parts are described more in detail below. All pipes between the different process steps were heated with heating tapes, controlled by temperature controllers, to a temperature needed to avoid condensation. The gas analysis and pyrolysis oil sampling is further described below.

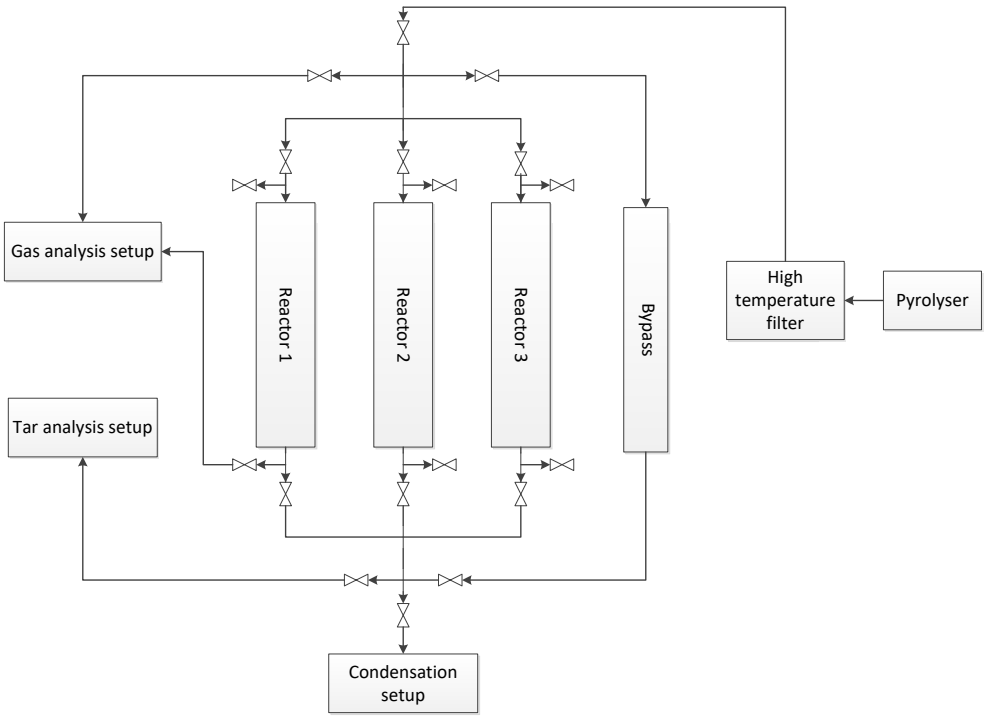


Figure 2 Schematics of the experimental setup at KTH

Pyrolyser

The pyrolysis gas needed for the experiments was produced in a fluidized bed pyrolyser equipped with a screw feeder for biomass feeding. This feeder is only leak free up to an overpressure of 5 kPa, and producing a too low driving force for the gas through all the process steps. Therefore suction pumps were also needed at the outlet after the reactors, because of pressure drops in the fluidized bed, high temperature filter and reactors.

Hot gas filter

The electrically powered filter unit, equipped with a ceramic filter, is constructed for removal of larger particulates from the gas stream before entering into the reactor. The ceramic filter temperature, monitored with three thermocouples coupled to temperature controllers can be operated to a temperature up to 700 °C. The filter vessel is also equipped with a purging system, enabling periodic purging with nitrogen gas to remove the filter cake on the ceramic filter, preventing a too large pressure drop and eventual plugging.

Catalytic reactors

The catalytic reactor setup, as schematically shown in Figure 2 is constructed to enable a separate operation of each of the three parallel-coupled reactors. Each cylindrical reactor has a maximum catalyst loading volume of 2.6 l. The reactor vessels and connecting pipes were heated by 19 temperature controlled heating tapes and heavily insulated to minimize heat loss from the system. Inert Duranit 1/8” balls were added to the bottom and top of the reactor in order to increasing

the thermal conductivity of the otherwise empty reactor space and allow for a precise placement of the catalytic bed to facilitate the inside top and bottom temperatures as well as the gas inlet temperatures to be monitored with the three pre-welded thermocouples.

Gas and pyrolysis oil sampling

A tar and gas sampling setup was built in order to analyse the change in gas and tar composition over the reactor. A schematic of the setup is shown in Figure 3. The sampling system includes three impinger bottle trains, equipped with three impinge bottles each. Two of the trains, at the inlet of the reactor system and after Reactor 1, were for cooling the pyrolysis gas with a temperature of 400 °C before the gas is further cleaned and before analysis of permanent gases. The 250 ml impinger bottles in these trains were half filled with water. The third train, sampling gas after the reactors, were for pyrolysis oil sampling from crude gas via the bypass and after conversion directly after the reactors. The two first bottles were filled with methanol and the last one with water. The bottles for tar sampling were placed in an ice-bath and the bottles in the other two trains were placed in water baths.

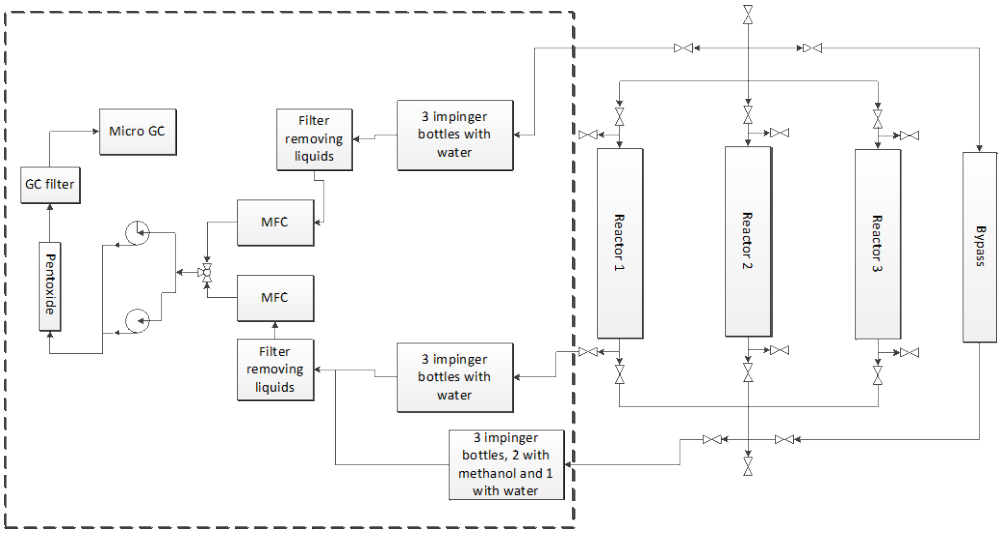


Figure 3 Schematics of the gas and tar analysis setup at KTH, shown inside the dashed line box to the left

3.2.2 Set-up at Cortus facility in Köping

A schematic view of the reactor setup is shown in the piping and instrument diagram in Figure 4. The setup was connected to the main pyrolysis vapour line of the Cortus pyrolyzer on site in Köping. Many of the components were the same as used at KTH, i.e. the filter unit and the three catalytic reactors setup. Sampling system for collecting oil samples was changed based on experiences from the tests carried out at KTH. Also, in this case, the pipes between different process steps were heated with heating tapes, controlled by temperature controllers, to a temperature needed to avoid condensation. The gas analysis and pyrolysis oil sampling is further described below.

The pyrolysis gas was initially fed from the main pyrolysis line through line a where larger particulates were removed in the ceramic filter. The filter was periodically purged with N_2 to prevent a build-up of particulates on the filter. The pyrolysis vapour flowed through line b where it was fed through one of the three parallel-coupled reactor units (R1-R3) where the conversion reactions were catalysed. The fourth column of the reactor setup is the bypass used when feed-through of pyrolysis gas or inert gas was required. The converted gas was fed back to the pyrolysis vapour line through line c where it was fed through to the burner.

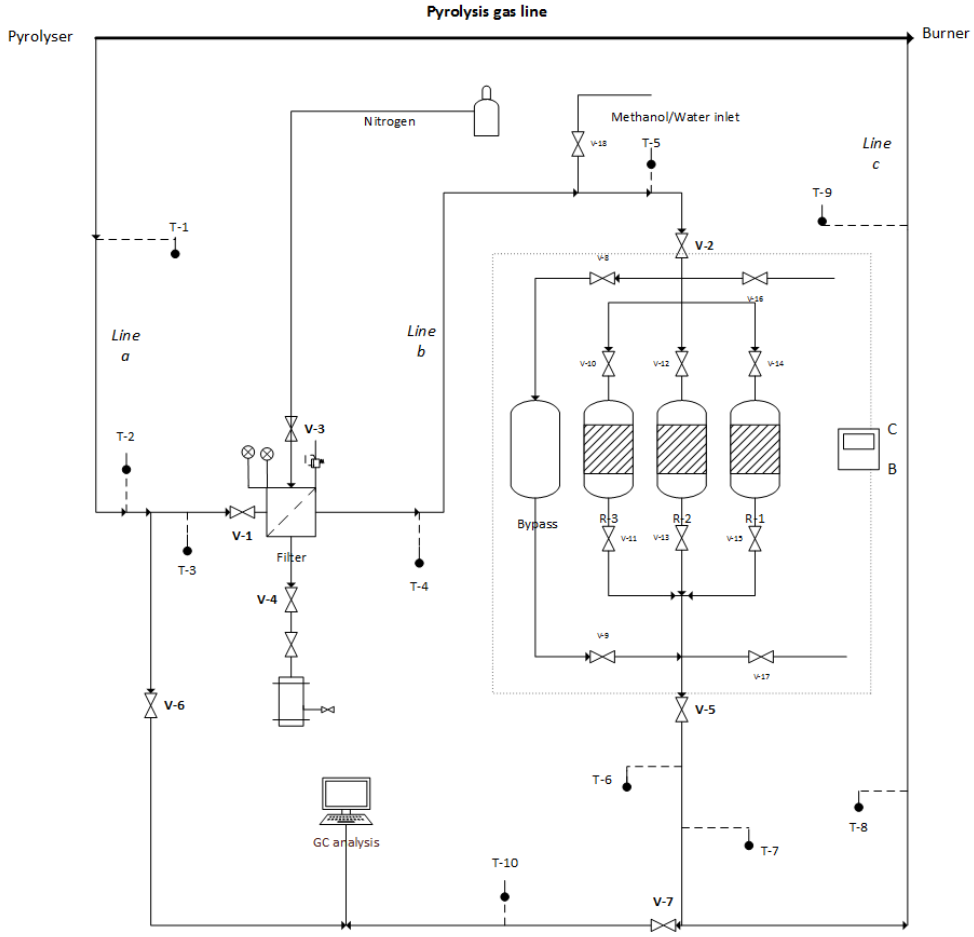


Figure 4 A schematic of the overall setup used at Cortus facility in Köping: T-*i* denotes heating tape-thermocouple pairs, V-*i* the valves while R-*i* are the reactors.

The pyrolysis vapour sampling system as shown in Figure 5 was fitted to the system, indicated by the GC analysis in Figure 4, to allow for continuous sampling of vapour upstream (V-6) and downstream (V-7) of the reactors. The system enabled both sampling of pyrolysis oil and determination of the composition of the permanent gases (H_2, CO, CO_2, CH_4) mixture at any given point of time with a micro gas chromatography (µ-GC) unit.

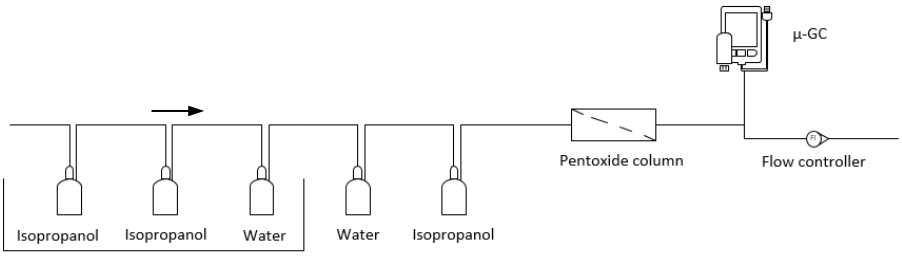


Figure 5 The gas and oil sampling setup: The bio oil is collected in the two first isopropanol impinger bottles in the cascade while the µ-GC measures the permanent gas components.

The sampling procedure for pyrolysis oil was a development of the procedure used at KTH, and in these tests, the first two and the last impinger bottles contained iso-propanol while the rest of the bottles in the sequence contained water. The three first bottles in the series were placed in a cooling water bath enabling condensation of the bio oil and preventing the iso-propanol from boiling. A pentoxide column, after the train, removed moist before the sample gas was introduced to the µ-GC.

To enable a burner test, the test system included a 20 kW Ecothal radiant tube burner from Sandvik. The burner is equipped with a series of thermocouples ($T_i = T_1 - T_7$) mounted along the tube, allowing for a relative monitoring of the combustion performance. T temperature of the chamber, $T_{chamber}$, is also monitored. All gas produced in the pyrolyser is combusted in the burner together with air. This allowed for a direct comparison of how well the gas is combusted in the burner.

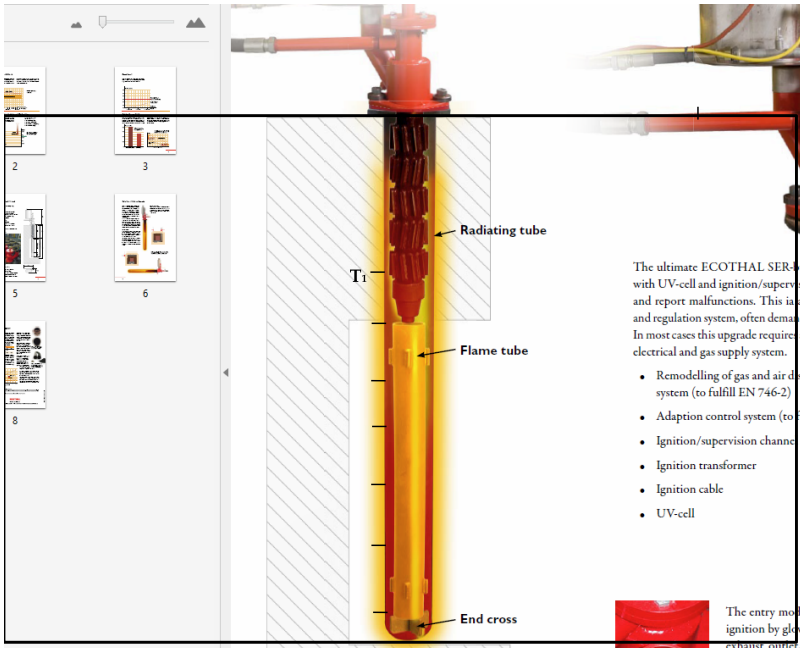


Figure 6 A schematic of the radiant tube burner installed in a chamber used for testing of the burner performance. The temperatures along the burner tube are monitored.

Thermocouple T_2 is located exactly at the burner nozzle where the combustion is assumed to start. A clear indication of the presence of a flame on the inside of the tube is when $T_i > T_{chamber}$.

3.3 EXPERIMENTAL PROCEDURES

3.3.1 Tests at KTH

The experimental conditions used in the tests are shown in Table 4.

Table 4: Conditions for the different vessels, with gas flows as for the test with the iron-based catalyst

	inlet	outlet	Temperature
Pyrolyser	0.9 kg/h biomass 2.15 m^3/h nitrogen	2.24 m^3/h pyrolysis gas	400 °C
High temperature filter	2.24 m^3/h pyrolysis gas	2.24 m^3/h particle free pyrolysis gas	420 °C
Reactor	2.24 m^3/h particle free pyrolysis gas	2.28 m^3/h converted pyrolysis gas	400 °C

The first test was made with the reactor filled completely with inert fillers. First all parts were heated with air flowing through the system to make sure everything worked well in sense of pressure drop, leaks and pumps. Biomass was thereafter fed into the pyrolyser and the experiment started. The experiment was running for over two hours with a few stops, due to a need for flushing the filter and improving the condensation setup. Since the pyrolyser was running for the whole time, the pyrolysis gas was vented off before the filter. During the experiment the temperature was logged and the gas composition at the inlet and outlet of the reactor was measured a total of nine times. Tar samples were taken from both the condensation setup and from the tar sampling setup.

During the heat up, in the tests using the Fe-based catalyst, the reactor was purged with nitrogen. When all parts were heated, biomass was fed into the pyrolyser and the experiment started. As for the inert test it was running continuously for about two hours, with two pauses for purging the filter. GC samples and bio-oil samples were taken continuously during the test, alternating between samples at the inlet and outlet of the reactor.

3.3.2 Tests at Cortus

The operation of the pyrolyser with GROT as the feedstock was performed using a set pyrolysis temperature of 380 °C. The provided pyrolysis vapour flow to the reactor unit varied between 2.5-3 Nm^3/h.

The temperature of the filter was maintained at 450 °C to prevent condensation of the pyrolysis oil while still removing large particles that had been transported with the fluid from the pyrolysis stage. The filter vessel was periodically purged with nitrogen (N_2) every hour throughout the experiment to remove the filter cake.

Heating tapes on pipes and valves were maintained at 450 °C during the actual test period to mitigate condensation and plug formation during operation. During standby between the actual test periods, the system was purged with a small nitrogen flow and kept at a temperature of around 200 °C.

Table 5 below shows the predetermined operational conditions of the experimental setup. The reactor units are denoted according to Figure 4 where reactor 1 (R1) remained unused, while essentially all of the uptime was spent on reactor 3 (R3). All the gas produced in the pyrolyser, 2.5 – 3 Nm^3/h, was diverted to the catalytic reactor setup during the test.

Table 5 Operational conditions for the experimental setup.

Unit	Catalyst	Bed volume [dm^3]	Temperature [°C]	Space velocity [h^{-1}]
R1	HT-25934	1.6	400-450	2500-3000
R2	Dolomite	1.0	450	2500-3000
R3	HT-25934	1.0	400-450	2500-3000

The initial step in the test, using a new iron-based catalyst, is the activation of the catalyst by exposure to the CO and H_2 in the pyrolysis gas. Since the activation is an exothermic process, the temperature was held at 400 °C during the activation period to avoid a possible peaking of the catalyst bed temperature above 500 °C in order to avoid unnecessary thermal sintering of the active material. The ramping rate during heating up of the catalyst bed was also held at 10 °C/min in order to mitigate any structural changes of the catalyst surface due to a to rapid temperature increase during the initial stages of heating. The temperatures of the catalytic bed were monitored at three different positions in the catalytic reactor: in the gas inlet as well as the top and bottom of the bed as shown in Figure 7 below. The space velocity varied between 2500-3000 h^{-1} depending on the flow rate.

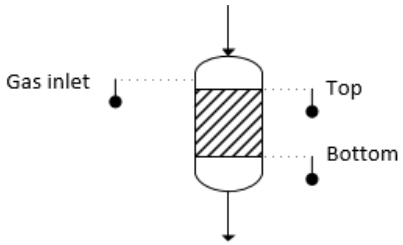


Figure 7 The temperature measuring point placement in the reactor for the reactor temperature profile.

In case of the dolomite catalyst, the material was pre-activated by calcination as described in Section 3.1.1 above.

3.4 CHARACTERIZATION AND ANALYSIS METHODS

The catalysts and pyrolysis products were analysed with a variety of different characterization methods as described below. For simplicity, the different methods used in the two test sites are separately described.

3.4.1 Tests at KTH

Only the permanent gases and pyrolysis oil samples collected during the tests were analysed.

Gravimetric

In the gravimetric tar analysis, the pyrolysis gas is bubbled through the tar analysis train indicated in Figure 3. A mass flow controller (MFC) measures the gas flow through the bottles to determine the total gas volume flowing through the bottles. The increase in weight of the bottles after flowing pyrolysis gas through them is a measure for condensed pyrolysis oil. By sampling gas directly after the reactor and through the bypass the amount of crude and converted could be determined and compared.

Karl-Fischer titration

The water content in the pyrolysis oil samples was determined by means of the ISO 6296 standard Karl-Fischer titration [33].

Permanent gases

The permanent gas composition was analysed with a micro gas chromatograph (Thermo Scientific, C2V-200) for both inlet and outlet of catalytic reactor as pointed out in Figure 3.

3.4.2 Tests at Cortus

The characterization and analysis were more extensive compared to the KTH tests and included analysis of permanent gases and pyrolysis oil samples as well as characterization of the surface of the catalysts used. Many of the methods used in the tests at KTH described above were also similarly used in the tests at Cortus plant in Köping.

Sampling of pyrolysis oil and permanent gas analysis

Sampling of pyrolysis oil were performed once per hour by switching the appropriate valve, feeding the gas sample through the 5 impinger bottles, containing isopropanol and water, as described in Section 3.2.2, to trap the pyrolysis oil. The condensed oil was stored in appropriate flasks in a fridge awaiting analysis. The flasks were weighed before and after the condensation of the oil to allow for a gravimetric study of the pyrolysis oil, similar as for the tests at KTH as described in Section 3.4.1.

The permanent gas composition was analyzed with the μ-GC after removal of the pyrolysis oils and residual moisture in the gas.

Characterization an analysis of pyrolysis oil samples

The condensed pyrolysis oil was characterized by means of Karl Fischer titration, as described in Section 3.4.1, as well as elemental analysis. The elemental analysis was performed according to ASTM 5291 standard [34] elemental analysis determined the C, H and O ratio of the oil.

Catalyst characterization

The catalysts were characterized before and after the tests at Cortus. The initial characterization to determine the active phase of the dolomite with XRD was performed using a Siemens D5000 X-ray diffractometer. Scattering angles (2Θ) between 10 to 90° with a step length of 0.020 °/s and a step time of 2 s was used.

The surface area of the Haldor Topsoe catalyst was determined with nitrogen adsorption (Micromeritics, ASAP 2000). The samples were outgassed by evacuation at 250 °C for a minimum of 4-5 h prior to analysis. Data were collected at liquid nitrogen boiling temperature (77 K). The surface area was thereafter calculated by the Brunauer–Emmett–Teller (BET) method.

The total sulfur and carbon content on the catalyst surface was determined by IR quantification of sample high-temperature oxidation in LECO, CS230 series and ELTRA, CS-2000 series instruments.

3.4.3 Mass Balance

A mass balance was developed in order to account for the carbon, hydrogen and oxygen in the process by evaluating the inlet (index in) and outlet (index out) streams on the basis of the carbon content. All inlet and outlet carbon streams as well as carbon accumulated on the catalyst surface is included in the mass balance. The accumulation of carbon on the catalyst surface is assumed to be linear to easily be able to account for the deposited carbon by discounting the mode of carbon build up.

$$N_{i,IN} = \int_0^t \dot{f}_{OUT}\, y_i M_{\mathrm{wi}} dt + \int_0^t x_i G_{OUT} dt + \Delta C \qquad (15)$$

$N_{i,IN}$ is the inlet mass, $\dot{f_{OUT}}$ is the total outlet molar flow of gas, y_i the molar fraction in the gas, M_{wi} is the molar weight of carbon, xi is the molar fraction in the oil and C_{OUT} is the outlet mass flow rate of the oil. The third term, ΔC, concerns carbon deposit on the catalyst in which the accumulation of carbon on the catalyst surface is determined by the total mass of the accumulated carbon

4 Results and Discussion

The experimental research was designed in such a way to possibly establish answers to some of the issues important for evaluating the suitability of the technology for further development to an industrial application. The issues of importance could be listed as follows:

- Is it possible to lower the condensation temperature of pyrolysis oil in the pyrolysis of at least 100 degrees from the level just below 400 °C?
- Is it possible to lower the amount of gravimetrically determined condensable pyrolysis oil by 50 % or more?
- Is it possible to activate the catalyst material directly in the process stream at the beginning of its use?
- What is the most suitable catalyst material? Metal-based or simple mineral based catalysts?
- What are the most appropriate process conditions, such as temperature and residence time, ratio for optimal reform of pyrolysis oil?
- How is the reforming catalyst affected by sulphur and other components in the gas? It is important to determine the need for sulphur removal or an alternative use of a sulphur resistant catalyst.
- How does surface carbon formation influence the catalyst performance?

4.1 TESTS AT KTH

The most important result of the experiments at KTH was finding that it is possible to activate the catalyst directly in the process stream. Activation is an exothermic reaction, which initially is displayed as a dramatic increase of the temperature of around 70 ° C in the bed, starting from a temperature slightly below 400 ° C. This is shown in Figure 8 for the temperature in the middle of the bed. To minimize catalyst thermal sintering, and thus loss of active surface area, it is important that the initial exposure to the process gas for activation is performed slowly in controlled way at as low temperatures as possible. This was important information prior to performing the tests in connection to the Cortus plant in Köping.

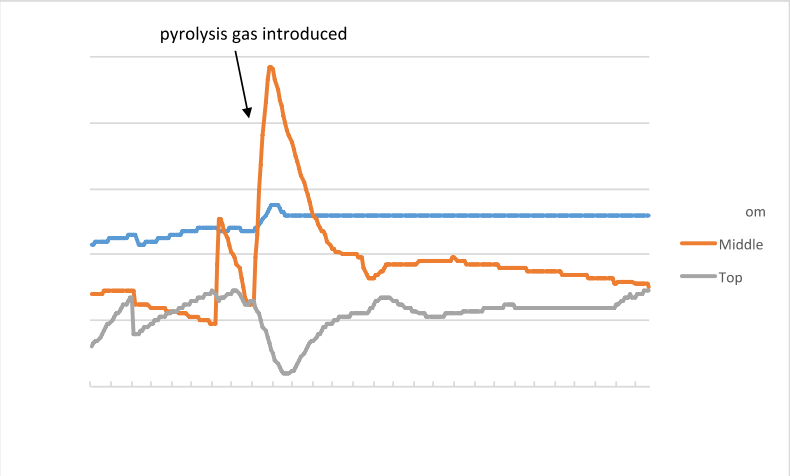


Figure 8 Temperature profiles inside the reactor during test using Fe-based catalyst.

The transformation of the pyrolysis gas in tests of KTH with the iron-based catalyst, showed relatively small changes after the reactor compared to the inlet crude pyrolysis gas. This may be due to the large dilution of the pyrolysis gas by the large amount of nitrogen gas used as fluidizing media in the fluid bed pyrolyser reactor (gas initially contains about 95 % nitrogen gas and pyrolysis residue). Table 6 illustrates how the gas composition changes where in particular the amount of hydrogen and carbon dioxide increases and carbon monoxide decreases after the conversion. It is however not clear if the observed changes are due to a conversion of the pyrolysis oil or if it is due to water gas shift, as shown in reaction 3, or a combination thereof, over the Fe-based catalyst.

Table 6 Permanent gas composition before and after the reactor in the tests at KTH.

	Inlet permanent gases **Molar flow rate (mol/h)**	**Outlet permanent gases** **Molar flow rate(mol/h)**
CO_2	1.590	2.53
CH_4	0.26	0.30
CO	1.69	1.40
H_2	0.44	1.63
Total	3.98	5.86

4.2 TESTS AT CORTUS PLANT IN KÖPING

Tests at Cortus plant in Köping were performed starting June 1 and ended July 6, 2016. The different results are subsequently described and discussed in the following sections.

4.2.1 Operational performance

The total accumulated exposure time of process gas to the iron-based, and dolomite catalyst, were 8 hours and 30 minutes, respectively. In the case of the dolomite, the test stopped after about 30 minutes because of bed collapse. The

dolomite material was very soft after calcination and both recarbonisation in the carbon dioxide-rich atmosphere, together with the high water content in the gas may affect the material further, rapidly compacting the bed. Due to the short operational time no results will be reported for the dolomite test. The low catalytic conversion temperature up to 500 ° C, which is far below the calcination temperature of 700-900 ° C, and the high carbon dioxide levels, indicate that lime-based materials in calcined form is not suitable as a catalyst material for the process.

The activation phase of the iron-based catalyst caused a sharp increase at the bottom temperature of the reactor, as illustrated by the blue curve in Figure 9. The shape of the temperature profiles is probably due to an overall exothermic activation of the catalyst, causing a sharply defined temperature gradient with elevated temperatures in the bottom of the reactor vessel, during the initial exposure, as the direction of flow forces the exothermically heated fluid downwards through the reactor vessel. The highest temperature reached was 489 °C. The temperature dip in the top of the reactor vessel may be attributed to endothermic reactions, occurring on the surface of the solid material at later stages of the activation phase of the surface. The temperature profiles, shown in in Figure 9, are rather smooth without the presence of short instantaneous thermal spikes, implying a smooth operation and stable flows.

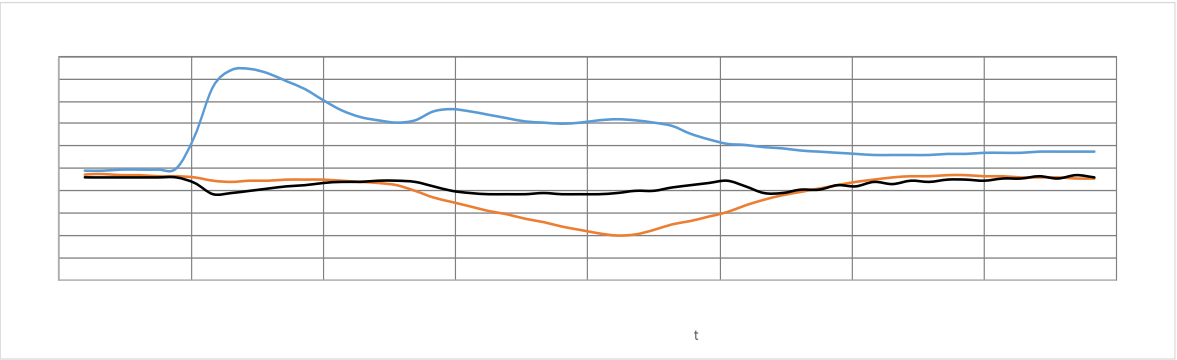


Figure 9 The temperature profile during start-up of reactor 3 (R3).

Examples of temperature profiles in the reactor during catalytic conversion using the activated catalyst is shown in Figure 10. The temperatures ranged between 420 and 450 °C at the top and bottom of the reactor, respectively, during exposure to a basically dust-free pyrolysis gas. The gas inlet temperature and the temperature in the bottom of the bed are close to each other. The temperature at the top of the bed is however lower, indicating an endothermic process, similar to catalytic conversion of heavy hydrocarbons into lighter.

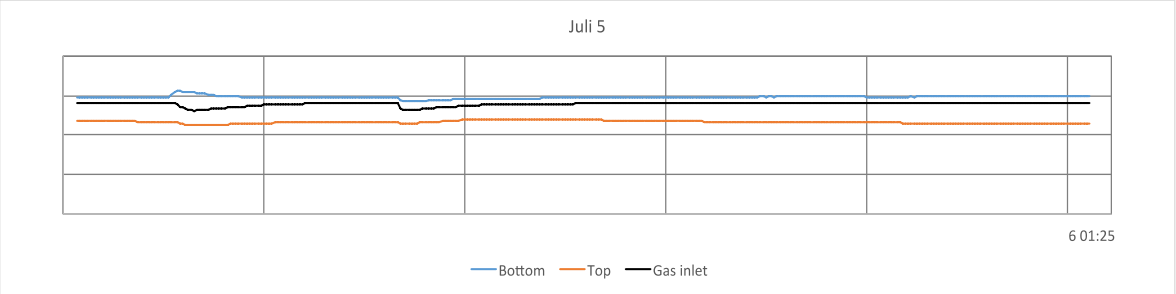


Figure 10 A temperature profile from one exposure event with reactor 3 (R3).

4.2.2 Pyrolysis vapour characterisation

To enable the evaluation of the catalytic conversion and activity a number of samples, regularly collected, and measurement of permanent gases were performed. The pyrolysis oil samples were thereafter characterised with different analysis methods, such as the mass flow rates of oil, followed by the oil and water content in the oil. The chemical composition of the pyrolysis oil was analysed by means of elemental analysis. The following sections describe the results from the sampling and chemical analysis of the pyrolysis oils and the permanent gases.

Fraction of pyrolysis oil and water

The amount of condensed water content in the pyrolysis gas is changed, as displayed in Table 7, increasing with approximately 65 %.

Table 7 The water content of the pyrolysis gas before and after the reactor based on Karl-Fischer titration

	Water content (kg/h)
Before the reactor	0.17
After the reactor	0.26

The amount of condensed oil per minute of flow for the inlet and inlet streams are presented in Table 8, where a significant decrease in gravimetric amount of pyrolysis oil per minute flow between the samples collected before and after the rector is observed. The observed reduction is 48 %.

Table 8 Gravimetric average amount of water free condensed pyrolysis oils collected per minute before and after the catalytic conversion.

	Condensed pyrolysis oil (kg/h)
Inlet stream before the reactor	0.66
Outlet stream after the reactor	0.32

Permanent gas analysis

The average molar flow composition of components of the permanent gases, CO_2, CH_4, CO, H_2, ethane, ethene and 1-butane, at the inlet and outlet of the reactor unit is shown in Table 9. The analysis was performed using the μ-GC.

The H_2 increases, and the CO decreases after the conversion. This could be due to a shift of the CO along with water by the water gas to CO_2, significantly increased after conversion, and hydrogen gas, as pointed out also in the case of the KTH tests above. However, the molar decrease of CO is smaller than the molar increase of CO_2, therefore, the observed changes in the concentrations of CO and H_2 cannot solely be explained by the water gas shift.

Table 9 Average molar flow composition of permanent gases at the inlet and outlet.

	CO_2	CH_4	CO	H_2	C_2H_4	C_2H_6	C_4H_8
Inlet gas before the reactor [mol/h]	10.57	1.05	6.14	0.63	0.14	0,15	0.05
Outlet gas after the reaktor [mol/h]	20.14	1.58	4.73	9.89	0.27	0.27	0.08

Pyrolysis oil analysis

Table 10 shows the elemental weight distribution of carbon, hydrogen and oxygen in the inlet and outlet pyrolysis oil streams, analysed according to the ASTM 5291 standard [34]. An evident decrease of the oxygen content is clearly observable, together with a simultaneous increase of the carbon content. The amount hydrogen is not significantly changed.

Table 10 The elemental analysis in terms of C, H and O of the untreated and treated oil sampled before and after the reactor, respectively.

	C (wt-%)	H (wt-%)	O (wt-%)
Oil sample before the reactor	50.3	4.9	44.8
Oil sample after the reactor	59.3	5.0	35.7

4.2.3 Catalyst characterization

Three physical aspects of the catalyst were analysed: The surface area, the carbon depositions on the iron-based catalyst surface as well as the active phase of the dolomite-based catalyst after curing.

The specific surface area

The surface area of the iron-based catalyst was determined with BET as described in Section 3.4.2. The surface area of the fresh catalyst was estimated to 71.9 m^2/g, to be compared to the lower values obtained for the spent catalyst as displayed in Table 11.

Table 11 Surface area [m^2/g] for the Haldor Topsøe catalyst. Samples from the top, middle and bottom of the reactor bed.

	Top	Middle	Bottom
Surface area [m^2/g]	39	35.2	34.4

The decrease of the surface area may be attributed to ageing of the catalyst where thermal effects cause a sintering of the material in the catalyst bed. The decreasing trend follows the temperature differences at the different bed heights as shown in Figure 10 with a low temperature of around 420 °C and a higher temperature of 450 °C in the top and bottom of the bed, respectively.

Carbon deposit on the catalyst surface

The chemical analysis of the amount of C on the iron-based catalyst displayed a not unexpected amount of carbon on the catalyst surface. The amount of carbon laydown on the catalyst surface shows an evenly distributed layer of carbon around 10 % by weight, as illustrated in Table 12, for samples collected in the top, middle and bottom of the catalyst bed. The catalyst showed nevertheless a good catalytic activity during the time the trial was on-going.

Table 12 Relative amount of carbon deposit on the iron-based catalyst surface for samples collected from the top, middle and bottom of the catalyst bed.

	Top	Middle	Bottom
Amount of carbon [wt-%]	10.8	10.2	9.7

TPO was used in order to further quantify and possibly also identify the form o carbonaceous deposits on the iron-based catalyst. Figure 11 shows the TPO results for the fresh catalyst (yellow curve) and used catalyst samples from the top (grey curve), middle (blue curve) and the bottom (orange curve) of the catalytic bed. The red curve shows the linear increase of the temperature during TPO, starting at a temperature of around 30 °C ending at a final temperature of 800 °C. The fresh catalyst indicates for carbon at three temperatures just below 100 °C, at around 250 °C and the last at around 750 °C. On the other hand, all used catalyst samples provide with a clear indication of carbonaceous depositions on the catalyst surface, as illustrated by the sharp peak at just below 450 °C in Figure 11 for the three samples collected in the top, middle and bottom of the catalyst bed.

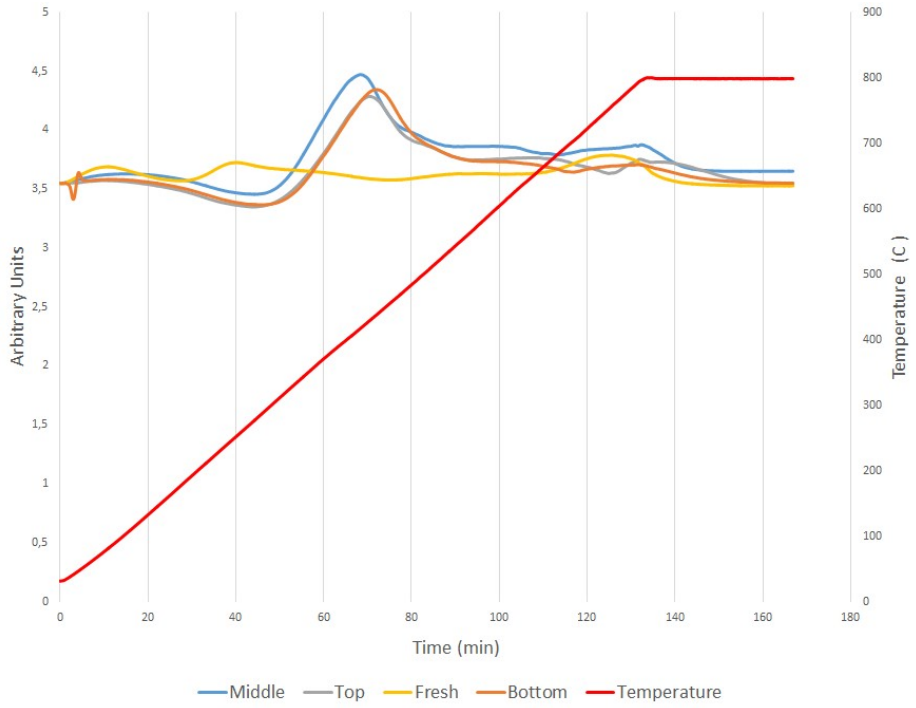


Figure 11 TPO curve for the fresh iron-based as well as for samples collected at the bottom, middle and top of the bed of used iron-based catalyst.

State of catalyst

The XRD analysis of samples from the top, middle and bottom of the catalyst bed, performed at Haldor Topsoe A/S, displayed catalysts were fully activated and with crystallite sizes of the active materials to be expected after typical use.

4.2.4 Combustion performance

The combustion tests were performed in a separate burner as described in Section 3.3.2. The tests included combustion using crude pyrolysis gas, as well as treated pyrolysis gas with 70 and 100 % load on the ejector, working as a pump to suck the pyrolysis gas through the system into the burner. Since excess of oxygen was used in all tests an oxygen of around 5.6 vol-% was measured in the flue gases from all tests.

During the combustion of the gas in the burner, a reduction of amounts of NOx/NO in the flue gas was observed for the treated gas, compared to the crude pyrolysis gas, as displayed in Figure 12.

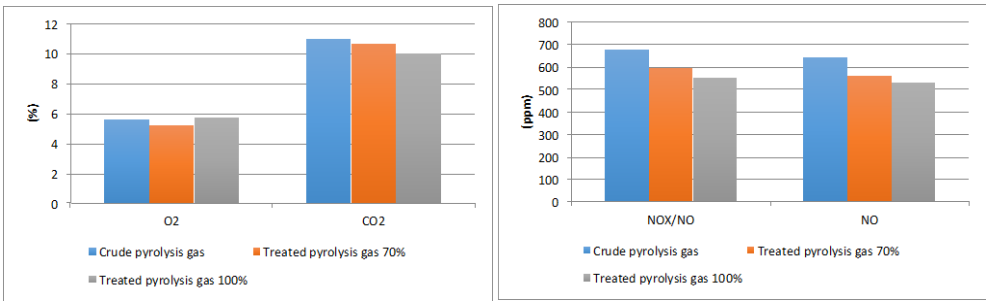


Figure 12 Gas composition in the flue gas after combustion of crude and treated pyrolysis gas. Left: O_2 and CO_2 and Right: NO_x + NO and NO.

Figure 13 shows temperature profiles along the radiant heat burner. From the profiles it is clear that the temperatures differs mainly for the two first temperatures T_1 and T_2 but thereafter for T_3 to T_7 more or less follows the same pattern. The T_5 to T_7 temperatures are the same as for the $T_{chamber}$, indicating that no flame is present in this zone of the tube. The radiant heat burner is designed for approx. 7 Nm^3/h. The flow introduced in the present tests was approx. 1.5-3.5 Nm^3/h, and therefore the flame length was shorter than the length of the tube. The temperature at the nozzle (T_2) is higher for the treated gas, compared to the crude pyrolysis gas, and is also higher than $T_{chamber}$, indicating that the combustion process started closer to the nozzle.

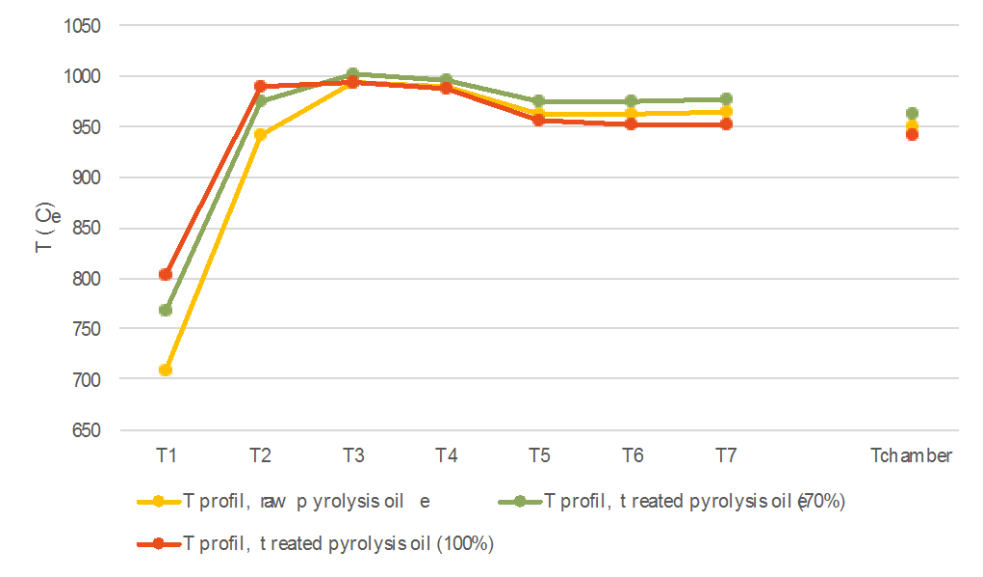


Figure 13 Temperature profiles obtained for crude and treated pyrolysis gas with the ejector on 70 and 100 % load.

4.3 CONCLUSIVE ANALYSIS AND DISCUSSION

The tests at Cortus test facility in Köping were performed using only a filter to remove particulates, mainly in form of pyrolytic residues, before the crude pyrolysis gas entered the catalyst reactor. The catalytic process still operated without any noticeable changes in catalytic activity, although carbon laydown was observed on the catalyst surface, a known deactivation mechanism for catalysts in this type of application [17]. Catalyst tolerant towards deactivation by carbon deposition, sulphur and sintering is a major target for converting biomass based pyrolysis oil. The present study, using an iron-based catalyst, shows a possible way forward. Nevertheless, important to keep in mind is the short exposure time and possible need for regeneration to remove e.g. carbon laydown and also possibly sulphur.

4.3.1 Catalytic conversion of the pyrolysis oil

The carbon balance of the process is an important indicator of how well the experiment is performed and monitored. By applying equation (15), described in Section 3.4.3, and results from Table 9, Table 10 and Table 12, it is possible to account for 95.6 %. The carbon balance indicates a good experimental performance with a high degree of monitoring of the process streams. The remaining carbon is assumed as lost during vent off through the side valve, opened during cool down of the reactor with N_2 or by soot passing out from the reactor system at higher N_2 flow rates.

A balance on the three major components of the stream; gas, oil and water is shown in Table 13.

Table 13 Mass balance of the permanent gas, oil and water in the pyrolysis vapor stream.

	Permanent gases [wt-%]	Pyrolys oil [wt-%]	Steam [wt-%]
Crude pyrolysis gas	44.5	44.4	11.1
Treated pyrolysis gas	65.5	19.0	15.5

The results in Table 13 show that the gas and water content increases between the inlet and outlet sample while the oil content decreases with 57 %. This is in agreement with 50 % reduction of oil between the inlet and outlet samples, obtained by gravimetric analysis of sampled oil, shown in Table 7. The increase in water content is probably attributed to hydrodeoxygenation of the bio oil, according to a similar mechanism as proposed by Dayton [25] in (7) and dehydration in (11).

Catalyst activity

Although only a limited exposure time was achieved in the test it may be worth mention the catalyst performance related to carbon formation evenly distributed on the catalyst at different levels of the reactor bed. The type of carbon formed at the surface is as described above in relation to Figure 11 a typical coke laydown, commonly formed at catalyst surfaces [35]. The catalyst nevertheless showed a good catalytic activity during the time the trial was ongoing.

Combustion performance

The combustion zone is longer for the treated pyrolysis gas compared to the crude pyrolysis gas, since it starts closer to the nozzle, as displayed by the thermocouple T_2 in Figure 13. This indicates a more rapid combustion of the treated pyrolysis gas resulting in a more evenly distributed temperature profile. The improved combustion performance may be related to the fact that the permanent gas molecules are smaller, compared to the larger vapour phase oils, and therefore have shorter residence time for complete combustion. There is a significantly higher content of permanents gas in the treated pyrolysis oil, as shown in Table 15, especially the hydrogen content. However, the effects of increased amount of hydrogen are not completely evident and may both as reported improve or impair the performance [36]. Also, the amount of oil is less, reduced by 57 wt-%, consisting also of lighter hydrocarbons, meaning that the total mass fraction of large oil molecules combusted are less for the treated pyrolysis gas. Another indicator for a better combustion performance is the lower NO_x levels in the flue gas after the burner in case of the treated pyrolysis gas. NO_x is normally produced at higher temperatures and may in the present case be formed in hot zones in the flame [37]. The lower NO_x for the treated pytolysis gas thus implies a more uniform combustion.

A more even combustion performance in the radiant tube burners subsequently implies an evenly distributed heat radiation from the tubes inside the gasifier reactor, which is importent for the overall performance of the reactor.

5 Conclusions

The tests at Cortus test facility in Köping were performed using only a filter to remove particulates prior to conversion of the crude pyrolysis gas in the catalyst reactor. The catalytic process still operated without any noticeable changes in catalytic activity, although carbon laydown was observed on the catalyst surface. The overall conclusion is that the results point in a positive direction, particularly in the case of the iron-based catalyst, where significant effects on the crude pyrolysis gas composition could be observed after catalytic conversion. The conclusions of the iron-based catalyst is as follows:

- A reduction in the amount of pyrolysis oil of approximately 57 % could be achieved in the tests.
- The gas volume increased significantly after the conversion.
- The composition of the pyrolysis oil also changed. For example, the amount of oxygen was dramatically reduced after the conversion. Implying less oxygenated compounds.
- The combustion of the gas in the radiant tube burner displayed a changed behaviour using the treated pyrolysis gas. Among other things, the levels of NO/NO_x were lower compared to when using the crude pyrolysis gas. The combustion started also closer to the burner nozzle, which means a longer flame.
- It is possible to activate the catalyst directly in the process flow, which is important in the development of the technology to an industrial process, because no additional surrounding system is required for the activation. We do however not know how good this method is since no comparison was made to an ideal catalyst activation procedure.

Given the results, further studies are recommended, including, among other things, investigations of the iron-based catalyst activity as well as transformations of the surface and material over time in more detail. Another important aspect to examine is the need for and a process for regeneration of the catalyst material in an industrial process.

6 References

1. R. Ljunggren, Process and Equipment for Producing Synthesis Gas from Biomass. WO2008073021A1, June 19, 2008.
2. R. Ljunggren, M. Amovic, P. Donaj, B. Moner, R. Alzuheri, Development of a fuel testing procedure for pyrolysis and gasification of various biomass fuels using TGA and WoodRoll® test plant, Svenskt Gastekniskt Center AB, 2014.
3. D. Mohan, C.U. Pittman, Jr., P.H. Steele. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. Energy & Fuels 20 (2006) 848-889.
4. S. Heyne, T. Liliedahl, M. Marklund, Biomass gasification - A synthesis of technical barriers for large scale deployment. Report 2013:5 Swedish Knowledge Centre for Renewable Fuels (f3), Gothenburg (2013) 76.
5. A.V. Bridgwater, Catalysis in thermal biomass conversion. Appl. Catal. A: General 116 (1994), 5–47.
6. M. Tripathi, J.N. Sahu, P. Ganesan, Effect of Process Parameters on Production of Biochar from Biomass Waste through Pyrolysis: A Review. Renew. Sust Energ. Rev. 55 (2016) 468-481.
7. H. Yang, R. Yan, H. Hanping Chen, D.H. Lee, C. Zheng, Characteristics of Hemicellulose, Cellulose and Lignin Pyrolysis. Fuel 86 (2007) 1781-1788
8. J. Piskorz, D.S Scott, D. Radlein, Composition of oils obtained by fast pyrolysis of different woods. In: Pyrolysis oils from biomass-producing, analyzing, and upgrading. American Chemical Society, ch. 16 (1988) 167–178.
9. P. Basu, Biomass gasification and pyrolysis: practical design and theory. Academic Press, Burlington, USA, 2010.
10. A. Oasmaa, D. Meier, Norms and standards for fast pyrolysis liquids 1. Round robin test. J. Anal. Appl. Pyrolysis 73 (2005) 323-4
11. G. Hochgesand, editor. Ullmann's encyclopedia of industrial chemistry; chap. Gas production. Wiley-VCH (2007) 1-169.
12. P.M. Mortensen, J.D Grünwaldt, P.A. Jensen, K.G. Knudsen, A.D. Jensen, A review of catalytic upgrading of bio-oil to engine fuel. Appl. Catal. A: General 407 (2011) 1-19.
13. T.S. Christensen, Adiabatic prereforming of hydrocarbons - an important step in syngas production, Appl. Catal. A: General 138 (1996) 285-309.
14. J.R. Rostrup-Nielsen, J. Sehested, J.K. Nørskov, Hydrogen and synthesis gas by steam- and CO_2 reforming. Adv. Catal. 47 (2002) 65-139.
15. J.R. Rostrup-Nielsen, Handbook of heterogeneous catalysis; chap. Steam reforming. Wiley-VCH (2010) 2882-2905.

16. K. Aasberg-Petersen, T.S. Christensen, I. Dybkjaer, J. Sehested, M. Østberg, A.P. Steynberg, et al. Fischer-Tropsch technology; chap. Synthesis gas production for FT synthesis. Elsevier (2004) 258-406

17. R. Trane, S. Dahl, M.S. Skjøth-Rasmussen, A.D. Jensen, Catalytic steam reforming of bio-oil. Int. J. hydrogen Energy 37 (2012) 6447 – 6472.

18. X. Hu, G. Lu, Comparative study of aluminasupported transition metal catalysts for hydrogen generation by steam reforming of acetic acid. Appl. Catal. B: Environment 99 (2010) 289-97.

19. D.A. Constantinou, J.L.G. Fierro, A.M. Efstathiou, A comparative study of the steam reforming of phenol towards H_2 production over natural calcite, dolomite and olivine materials. Appl. Catal. B: Environment 95 (2010) 255 - 69.

20. D. Sutton, B. Kelleher, J.R.H. Ross, Review of literature on catalysts for biomass gasification. Fuel Processing Technology 73 (2001) 155–173.

21. K. Sasaki, X. Qiu, Y. Hosomomi, S. Moriyama, T. Hirajima, Effect of Natural Dolomite Calcination Temperature on Sorption of Boroate onto Calcined Products. Microporous and Mesoporous Materials 171 (2011) 1-8.

22. C_J. Chen, W-S. Lee, A. Bhan, Mo_2C Catalyzed Vapor Phase Hydrodeoxygenation of Lignin- derived Phenolic Compound Mixtures to Aromatics under Ambient Pressure. Appl. Catal. A: General 510 (2015) 42-48.

23. R. Olcese, M.M. Bettahar, B. Malaman, J. Ghanbaja, L. Tibavizco, D. Petitjan, A. Dufour, Gas-phase Hydrodeoxygenation of Guaiacol over Iron-based catalysts. Effects of Gases Com- position, Iron Load and Supports (Silica and Activated Carbon.) Appl. Catal. B: Environmental 129 (2012) 528-538.

24. N.T.T. Tran, Y. Uemura, S. Chowdhury, A. Ramli, Vapor-phase Hydrodeoxygenation of Guaiacol on Al-MCM-41 Supported Ni and Co Catalysts. Appl. Catal. A: General 512 (2015) 93-100.

25. D.C. Dayton, R.P. Gupta, B.S. Turk, A. Kataria, J.P. Shen, Catalytic Biomass Pyrolysis Process. WO2013134391A1, September 12, 2013

26. Y. Han, D.N. McIlroy, A.G. McDonald, Hydrodeoxygenation of Pyrolysis Oil for Hydrocarbon Production using Nanospring Based Catalysts. J. Anal. Appl. Pyrolysis 117 (2016) 94-105.

27. G.S. Foo, A.K. Rogers, M.M. Yung, C. Sievers, Steric Effect and Evolution of Surface Species in the Hydrodeoxygenation of Bio-Oil Model Compounds over Pt/HBEA. ACS Catal. 6 (2016) 1292-1307.

28. J.E. Peters, J.R. Carpenter, D.C. Dayton, Anisole and Guaiacol Hydrodeoxygenation Reac- tion Pathways over Selected Catalysts. Energy&Fuels 29 (2015) 909-915.

29. B. Rozmysłowicz, P. Mäki-Arvela, D.Yu. Murzin, Fatty Acids-Derived Fuels from Biomass via Catalytic Deoxygenation, in Biomass Conversion: The Interface of Biotechnology, Chemistry and Materials, Eds C. Baskar, S. Baskar, R.S. Dhillon, Springer-Verlag Berlin Heidelberg (2012) p. 199.

30. E. Furminsky, F.E. Massoth, Deactivation of Hydroprocessing Catalysts. Catal. Today 52 (1999) 381-495

31. R.L. Bates, J.A. Jackson, Dictionary of geological terms, Third edition, Anchor Books, Random House Inc. New York, 1984.

32. I. Ávila P.M. Crnkovic F.E. Milioli K.H. Luo, Thermal decomposition kinetics of Brazilian limestones: effect of CO2 partial pressure, Environ. Techn., 33(10) (2012) 1175–1182.

33. ISO 6296:2000, Petroleum products -- Determination of water -- Potentiometric Karl Fischer titration method. http://www.iso.org/iso/catalogue_detail.htm?csnumber=27593

34. ASTM D5291, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants. http://www.astm.org/Standards/D5291

35. C.H. Bartholomew. Mechanisms of catalyst deactivation. Appl Catal A: General 212 (2001) 17-60.

36. Y. Karagöz, T. Sandalcı, L. Yüksek, A.S. Dalkılıç, S. Wongwises, Effect of hydrogen–diesel dual-fuel usage on performance, emissions and diesel combustion in diesel engines. Adv. in Mech. Engineer. 8(8) (2016) 1–13.

37. P.F Barry, S.L. Somers, S. Londerville, Duct Burners in The John Zink Hamworthy Combustion Handbook, Second Edition: Volume 3, Ed. C.E. Baukal Jr, CRC Press, Taylor & Francis Group (2014) p. 93.

CATALYTIC CONVERSION OF PYROLYSIS GAS IN THE WOODROLL® PROCESS

Gasification of biomass is an attractive solution for renewable production of alternative fuels, energy gas and chemicals. The WoodRoll®-process is a novel technology for biomass gasification which is divided into three steps – drying, pyrolysis and gasification. The biggest challenge for the commercialization of the process is the integration of all the process steps in a continuous process. The produced pyrolysis gas, combusted to provide the heat for the entire process, consists of a large fraction of heavy hydrocarbons in the form of condensable oil or tar. Lighter hydrocarbons are beneficial for the process implying less expensive process equipment for handling the pyrolysis gas.

The project considered direct catalytic reforming of the pyrolysis oil in the pyrolysis gas into lighter oils with lower condensation temperature or to gas molecules. In summary, the results indicate a great potential. Catalytic conversion was carried out, maintaining the catalytic activity, when exposed to a real oil-rich pyrolysis gas, with only particulate filtration prior to the catalyst. A 57 % reduction in the amount of pyrolysis oil could be achieved with a simultaneous significant increase in gas volume. Also, improved combustion performance with lower levels of NO/NOx with a more rapid and uniform combustion was accomplished.

Energiforsk is the Swedish Energy Research Centre – an industrially owned body dedicated to meeting the common energy challenges faced by industries, authorities and society. Our vision is to be hub of Swedish energy research and our mission is to make the world of energy smarter!

Energiforsk