Green Birds project

final report

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Green Birds (5.2818) is a project carried out within the framework of the TKI BBE Innovation projects devoted to the co-production of bioenergy and green chemicals from biomass gasification. The project was carried out by Avantium, ECN and Kodok between January 2014 and December 2015. Green Birds was financed by the Dutch Ministry of Economic Affairs under reference TEBE113008.

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Abstract

Green Birds (TEBE 113008) is a project carried out within the framework of the TKI BBE Innovation projects carried out by partners Avantium, ECN and Kodok in 2014-2015, and funded by the Dutch Ministry of Economic Affairs under reference TEBE113008.

The Green Birds project aims to increase the technical and economic feasibility of the co-production of energy/fuels and green chemicals from thermochemical conversion of biomass. Producer gas from gasification of wood and other lignin-rich feedstock contains significant concentrations of high-value compounds such as BTX (benzene, toluene, and xylenes) and ethylene. The smart idea of Green Birds is the capture and recovery instead of the costly conversion of these valuable compounds from producer gas. This approach results in an increase of the overall efficiency of the conversion process as well as an improvement of the economic viability of bioenergy plants.

In order to reach this goal, several strategies have been applied. On the one hand, the use of lignin-rich feedstock has been evaluated for the increase of the yield of high-value compounds (BTX, ethylene) during gasification. Moreover, the valorization of humins (residue from biorefinery processing) via thermochemical processing has been studied, including strategies to overcome the challenge of feeding this residue to the reactor. In parallel, technologies and processes have been developed for the implementation of separation of BTX and ethylene from producer gas (absorption, adsorption, and reactive separation processes) in biomass gasification plants. A number of co-production schemes have been selected for a techno-economic evaluation to determine the effect of the implementation of co-production technologies on the production cost of bio-SNG. Green Birds resulted in the first proof of principle of co-production technologies. This report summarizes the main results obtained in the framework of this project.

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Nomenclature

AROM	Mixed aromatics
BTX	Benzene, toluene and xylenes
DDB	Dried distilled biomass
DEA	Dilute ethylene aromatization
EB	Ethylbenzene
SNG	Synthetic natural gas
USD	American dollar

Samenvatting

Ethyleen en benzeen zijn slechts een klein deel van het totale volume van biomassavergassinggasgas (ca. 5 vol.%), maar ze zijn verantwoordelijk voor ongeveer 25% van de energie-inhoud van het gas. In de route naar SNG productie zijn ze schadelijk voor de gebruikte katalysatoren. Dit is een reden om in het SNG proces een reformer op te nemen die deze componenten omzet in syngas. Echter, ze hebben een hogere economische waarde dan het eindproduct, SNG. Het afscheiden van benzeen en ethyleen uit stookgas is een veelbelovende optie die de weg opent voor de coproductie van brandstoffen en groene chemicaliën vanuit biomassa(rest)stromen via vergassing.

Dit is de basis voor het Green Birds project met als doel het verhogen van de technische en economische haalbaarheid van de coproductie route van energie, brandstoffen en groene chemicaliën uit biomassa. Het innovatieve van Green Birds is het afvangen en het oogsten van de waardevolle verbindingen in plaats van de (kostbare) omzetting van deze verbindingen naar CO, H_2 en CH_4. Deze aanpak resulteert in zowel een toename van de totale energie efficiëntie van het conversie proces als een verbetering van de economische haalbaarheid van bio-energie installaties. Om dit doel te bereiken zijn verschillende strategieën toegepast in het kader van het project. Aan de ene kant zijn technologieën en processen ontwikkeld voor de toepassing van BTX (Benzeen, Tolueen en Xyleen)- en ethyleen scheiding. Aan de andere kant is dit technische werk aangevuld door een markt analyse om een compleet beeld over productievolumen, prijzen, kwaliteit en concurrentie van bio-BTX en bio-ethyleen. Het uiteindelijke resultaat van het project is een beslissing voor de schaalvergroting en de demonstratie van de technologieën ontwikkeld tijdens het project.

De eerste optie om het coproductie schema te verbeteren is de toename doelverbindingen (BTX en ethyleen) tijdens vergassing te onderzoeken. Verschillende experimenten werden uitgevoerd om te bepalen of er een correlatie is tussen het ligninegehalte van de biomassa brandstof en de opbrengst van BTX en ethyleen. Daarvoor is een lignine-rijke brandstof uit een bioraffinage process (dried distilled biomass, DDB) gebruikt tijdens vergassingtesten van een mengsel met hout. Hout werd vervangen door DDB (i.e. waarbij het lignine gehalte van 20 wt.% naar 50 wt.% stijgt), daalt het CO gehalte van stookgas van 35 vol.% naar 30 vol.%, de benzeen concentratie stijgt van 8,600 ppmv naar 12000 ppmv, ethyleen stijgt van 4.2 vol.% naar 5.8 vol.%, en de H_2S concentratie neemt van 250 ppmv naar 2500 ppmv toe. Echter, wanneer opbrengsten geëvalueerd worden (dus de conversie wordt meegenomen), is er alleen een variatie van CO en ethyleen waar te nemen. De CO opbrengst daalt lineair van 0.35 kg/kg naar 0.25 kg/kg, terwijl de ethyleen opbrengst toeneemt van 0.04 kg/kg naar 0.05 kg/kg in de rang van geteste brandstofsamenstellingen.

Het Green Birds project heeft ook de thermochemische valorisatie van humine onderzocht, als potentiele bron voor de coproductie van groene chemicaliën. Humines zijn een heterogeen, half-

solide, stroperig nevenproduct geproduceerd in Avantium's YXY bioraffinageproces. Deze brandstof vormt een grote uitdaging, vooral bij de voeding en vanwege zijn gedrag tijdens opwarmen. Humines verbranding in een drop-tube reactor met het gebruik van een eigen voedingssystem was uiteindelijk succesvol door een hoge mate van verneveling van de brandstof. Wel ontstaan er afzettingen vanwege de hoge concentratie van natrium in het brandstofmateriaal. Vergassingtesten zijn ook uitgevoerd in de MILENA vergasser. Het voeden van humines is uiteindelijk gelukt, maar er ontstonden schuimproblemen binnen de reactor. Het schuimen veroorzaakte op zijn beurt de verstopping van de interne circulatie van bedmateriaal tussen de combustor en de riser. Het vergassen van humines op lab schaal is uitdagend, maar niet onmogelijk. Ook is geconstateerd dat het gebruik van alkalivangers (zoals bij voorbeeld aluminosilicaten) nodig zijn om het probleem van hoge natriumconcentraties in de brandstof te ondervangen. Een andere strategie die bekeken is om humines te voeden is gebaseerd op het impregneren/mengen van humines op een poreus dragermateriaal zoals hout of klei. Hiervoor is een mengsel van 25 wt.% humine met beukenhout bereid voor vergassingtesten. Additionele oventesten werden uitgevoerd door het mengen van lignine en humines met een hoge-poreuze klei in verschillende verhoudingen (30 wt.%, 50 wt.%, en 70 wt.% humines) om het smelten- en schuimen gedrag van de mengsels te studeren. De resultaten van de experimenten lieten zien dat mengen een haalbaar alternatief voor de voeding van humins naar een verbrandings- of vergassingsinstallatie. Ondanks deze eerste goede resultaten, is verder werk noodzakelijk voor de optimalisering van deze strategie. Daarnaast zou verder werk moet nagaan over verbeteringen van het reactor ontwerp om te kunnen omgaan met deze uitdagende biogene afvalstroom.

Daarnaast zijn er een tweetal technologieën ontwikkeld binnen Green Birds voor de afvangst en oogst van BTX en ethyleen uit stookgas. ECN heeft hiervoor een BTX scrubbingsysteem ontwikkeld gebaseerd op een absorptie vloeistof. Tijdens eerste experimenten met stikstof als strippergas, werden en BTX afvangst van meer dan 90% bereikt. Bij verdere testen werd stoom gebruikt als strippergas en is door middel van condensatie een zuivere BTX stroom verkregen. Een belangrijke mijlpaal is bereikt in november 2014, waarbij > 1 kg bio-BTX werd geoogst uit stookgas van biomassa vergassing. Het bio-BTX product bevatte ~87 wt.% benzeen, 6.5 wt.% tolueen en sporen van andere verbindingen (xyleen, styreen, naftaleen). De verwijderingsefficiëntie kwam uit op ~ 94% bij een stoomdebiet van 820 g/uur. Als het stoomdebiet van 820 g/uur naar 205 g/uur daalt (i.e. ¼ van het initieel debiet), nam de efficiëntie af naar 82%. De experimentele resultaten zijn daarnaast gebruikt voor de validatie van de absorptie/stripping model.

De tweede technologische ontwikkeling is de afscheiding van bio-ethyleen uit stookgas. Daarvoor heeft Avantium gewerkt aan de ontwikkeling van geschikte adsorbentia. Een eerste screening studie van verschillende commerciële zeolieten toonde dat lage Si/Al zeolieten zoals X- en A typen goede ethyleen adsorptie materialen bleken te zijn. A-type zeoliet werd verrijkt met verschillende alkali-, aardalkali- en transitiemetalen. Van de geteste functionele zeolieten is de grootste adsorptiecapaciteit gevonden bij [Ca]A en [Ag]A materialen, met tot 7 wt.% ethyleen geadsorbeerd op 40°C en 5 bar. Eerste testen toonden dat adsorptie van [Ca]A negatief beïnvloedt wordt door de aanwezigheid van water in stookgas. Daarnaast werden ethaan en CO_2 ook gecoadsorbeerd op het materiaal. Ter vergelijking kan [Ag]A selectief ethyleen adsorberen. Echter, daar is een regeneratie/desorptie stap bij 200°C nodig om 80% van de originele adsorptiecapaciteit van [Ag]A te herstellen. Bovendien werd een vermindering van de selectiviteit en capaciteit van [Ag]A geobserveerd over meerdere adsorptie/desorptie cycli. De 2 geselecteerde sorbentia ontwikkeld door Avantium, [Ca]A en [Ag]A, zijn bij ECN getest onder relevante vergassingcondities. De resultaten van deze testen waren consistent met de eerste resultaten verkregen door Avantium. Tijdens de test met [Ca]A zeoliet, steeg de bed temperatuur van 30°C tot 90°C. Daarnaast werden ethyleen, ethaan, acetyleen en CO_2 co-geadsorbeerd. Na 10 minuten bedrijf, vond de doorbraak van CO_2 plaats, en kort daarna ook de doorbraak van de

waterkoolstoffen. Acetyleen is de sterkste geadsorbeerd verbinding. Tijdens desorptie werd 70-90% van de geadsorbeerde ethyleen en CO_2 vrijgelaten. Het experiment met [Ag]A zeoliet liet zien dat het materiaal ethyleen en acetyleen afvangt, maar geen ethaan. [Ag]A adsorbeert geen CO_2, maar het kan wel CO afvangen. Tijdens het experiment waren er sporen van de reductie van zilveroxide via de reactie met H_2 en/of met CO. Na verloop van tijd werd een deel van de geadsorbeerde CO weer vrijgelaten, die met zuurstof van het zilveroxide reageert om CO_2 te vormen. Er waren ook sporen van katalytische activiteit van de [Ag]zeoliet voor exotherme reacties zoals methanisatie, hydrogenatie en waarschijnlijk ook WGS en/of CO disproportionering, waarbij ethaan en methaan worden geproduceerd. Al met al toonden de experimenten dat verder onderzoek nodig is voor de ontwikkeling van ethyleen sorbentia. Daarbij is het belangrijk om de hoofdcomponenten van stookgas in de gaten te houden. Acetyleen is vooral interessant, omdat het sterker dan ethyleen gebonden wordt. Het experiment met [Ag]A toonde dat het beladen van de zeoliet met een metaal dat met stookgas kan reageren, of dat zelfs als katalysator kan fungeren, een riskante optie is.

Binnen Green Birds is ten slotte ook gekeken naar de route van reactieve scheiding, waarbij benzeen en ethyleen omgezet worden in producten die makkelijker af te scheiden zijn en ook een extra economische waarde hebben. Uit een eerste screening van mogelijke processen werden ethylbenzeen productie en ethyleen aromatisering geïdentificeerd als de meest veelbelovende routes. Deze geselecteerde routes zijn getest op lab schaal. De resultaten lieten zien dat een hoge ethyleen conversie, >90%, mogelijk is. Hogere temperaturen begunstigen de productie van lichtere aromaten, met een hogere benzeen concentratie in het inlaatgas verschoof de productdistributie naar ethylbenzeen. Gebaseerd op de experimentele resultaten werden verschillende coproductie schema's gemodelleerd en geanalyseerd ten opzichte van de referentie, het SNG proces. De economische evaluatie toonde dat alle bestudeerde coproductie routes leiden tot een verlaging in de productiekosten van bio-SNG met 5-20% ten opzichte van de referentie SNG case. Verdere verlaging van kosten kan bereikt worden door bij voorbeeld opschaling van productie, gebruik van goedkopere biomassa brandstoffen of de verhoging van doelverbindingen tijdens het vergassingsproces. Deze opties zijn verder gestudeerd binnen het Blue Bird project.

Summary

Ethylene and benzene make only a small part of the total volume of producer gas (~ 5% vol.), but together they account for ~25% of the gas energy content. These compounds not only have a detrimental effect on catalysts e.g. in SNG production, but they have also a higher economic value than the main product, SNG. Thus, the separation and recovery of benzene and ethylene from producer gas is a promising option that opens up the way for the co-production of fuels and green chemicals from biomass gasification.

With this background, the Green Birds project aims to increase the technical and economic feasibility of the co-production of energy/fuels and green chemicals from thermochemical conversion of biomass. The smart idea of Green Birds is the capture and recovery instead of the costly conversion of these valuable compounds from producer gas. This approach results in an increase of the overall efficiency of the conversion process as well as an improvement of the economic viability of bioenergy plants. In order to reach this goal, several strategies have been applied within the framework of the project. On the one hand, technologies and processes have been developed for the implementation of separation of BTX and ethylene in biomass gasification plants. This technical work has been complemented with an extensive market analysis in order to provide a complete picture on competition, volumes, prices and quality of bio-BTX and bio-benzene. The final outcome of the project is a decision for the scale-up and demonstration of the processes and technologies developed within the project.

The first approach considered is the increase in the yield of benzene and toluene during gasification. For this, different experiments have been carried out to determine whether there is a correlation between the lignin content of the gasification fuel and the yield of target compounds. A lignin-rich fuel (dried distilled biomass, DDB) was used in gasification tests in mixtures with wood. When switching wood by DDB (i.e. increase in lignin content from ~20wt.% to 50 wt.%), CO concentration decreased from 35% vol. to 30% vol. (dry basis), C_6H_6 increased from 8,600 ppmv to 12000 ppmv, ethylene slightly increased from 4.2% vol. to 5.8% vol., and the H_2S increased from 250 ppmv to 2500 ppmv. However, when evaluating yields (which consider variations in both gas composition and carbon conversion), only CO and ethylene show a significant variation with the composition of the solid feedstock. CO yield decreases linearly from 0.35 to 0.25 kg/kg and ethylene yield increases from 0.04 to 0.05 kg/kg in the range of compositions tested.

Green Birds has also studied the valorization of humins (a carbonaceous, heterogeneous, syrup-like by-product of biorefinery process) via thermochemical conversion as a potential source for the production of green chemicals. This feedstock poses a big challenge, particularly its feeding and its behaviour during heating up. The combustion of humins in a drop-tube reactor using an in-house feeding system was eventually successful by sufficient atomization of the fuel. However, deposits occurred due to the high concentration of sodium in the material. Gasification tests in the MILENA

gasifier were also performed. Although the feeding of humins was successful, problems arose within the reactor related to foaming, which in turn caused the blockage of the internal circulation of bed material between the combustor and the riser zones. All in all, the gasification of humins at lab-scale proved challenging, but not unfeasible. On the other hand, due to the high concentration of sodium in the fuel, which eventually leads to problems of deposits, corrosion and agglomeration, it would be necessary to use a 'getter' material (e.g. dolomite, aluminosilicates) in the bed in order to bind the sodium to less troublesome compounds. Another approach explored within this project to overcome the feeding challenges of humins was based on the impregnation/mixing of humins on a porous carrier like wood and clay. For this purpose, a mixture of 25 wt.% humin in beech wood was prepared for gasification testing. Additional oven tests were performed by mixing lignin and humin with a high-porous natural clay (sepiolite) in different ratios (30%, 50%, and 70% wt.) in order to investigate its melting/foaming behavior. The results of these experiments showed that mixing is a feasible alternative in order to properly feed humins into a gasifier or a combustor. However, despite the valuable information obtained, further work would be required for the optimization of this strategy. Moreover, future work should explore improvements in the reactor design to cope with this troublesome feedstock.

Technologies have also been developed for the capture and recovery of BTX and ethylene from producer gas within the project. In the former case, ECN has developed a BTX scrubbing system using a liquid absorption medium. During preliminary experiments with N_2 as stripping gas, benzene removal over 90% was achieved. Further tests implemented steam in the stripper for the further recovery of the removed bio-BTX by condensation as a product. An important milestone for bio-BTX recovery was reached in November 2014, where > 1 kg BTX was harvested for the first time from biomass gasification producer gas. The BTX product contained ~87% benzene, 6.5% toluene and traces of other compounds (xylenes, styrene, naphthalene…). The removal efficiency kept around 94% when operating the stripper with 820 g/h. Decreasing the stripping steam to ¼ of the initial flow made the efficiency drop to 82%. The experimental results were used for the validation of the absorption/stripping model.

In the case of removal of ethylene from producer gas, adsorption processes have been developed. For this, Avantium has worked on the development of suitable sorbent materials. A preliminary screening of different commercial zeolites showed that low Si/Al types, such as X and A, were good ethylene sorbents. Zeolite A was exchanged with different alkali, alkali earth and transition metals. Among the functional zeolites tested, the largest ethylene adsorption capacities were found for zeolite [Ca]A and [Ag]A, with up to 7wt% ethylene adsorbed at 40 °C and 5 bar. First tests showed that the adsorption of [Ca]A is affected by the presence of H_2O in the producer gas. Moreover, ethane and CO_2 were co-adsorbed by the material. In comparison, [Ag]A was able to selectively adsorb ethylene. However, a regeneration/desorption step at 200 °C is needed to recover 80% of the original ethylene adsorption capacity of [Ag]A. Moreover, a decrease in ethylene adsorption selectivity and capacity was observed over several adsorption-desorption cycles. The 2 selected sorbents developed by Avantium, [Ca]A and [Ag]A, were delivered to ECN for testing under realistic gasification conditions. The results obtained were in general consistent with the preliminary results obtained by Avantium. During the test with Ca-zeolite, the bed temperature increased from 30°C to 90°C. Ethylene, ethane, acetylene and CO_2 were co-adsorbed. After 10 minutes, the breakthrough of CO_2 took place, and soon after the breakthrough of the rest of hydrocarbons. Acetylene is the most strongly adsorbed compound. During desorption, 70-90% of the adsorbed ethylene and CO_2 is released. The experiment with the Ag-zeolite showed that the material is able to capture ethylene and acetylene, but not ethane. [Ag]A does not adsorb CO_2, but it does adsorb CO. There were signs of reduction of the silver oxide via reaction with H_2 and/or CO. After some time, part of the adsorbed CO is released, which reacts with oxygen from the silver

oxide to form CO_2. There were hints of catalytic activity of the Ag-zeolite towards exothermal reactions e.g. methanation, hydrogenation and possibly WGS and/or CO disproportionation, where ethane and methane are formed. All in all, the experiments showed that further research is needed in sorbent development. For this, it is important to pay attention to all the main components of producer gas. Acetylene is particularly interesting, since it is bound to the sorbent more strongly than ethylene. The test with [Ag]A showed that it is a risky option to load the zeolite with a metal that can react with producer gas or that could even act as a catalyst.

Green Birds has also explored the route of reactive separation, which transforms benzene and ethylene into products that are easier to separate and add extra economic value. From a screening process, ethylbenzene production and aromatization of ethylene were identified as the most promising pathways based on criteria of added value, capital and operating costs, and process integration. These promising pathways were experimentally tested. The experiments indicated that high ethylene conversion > 90% are achievable, whereas ~40% ethylene was converted to aromatics. Higher temperatures favour the production of lighter aromatics, whereas higher concentration of benzene at the inlet shifts the product distribution towards ethylbenzene. Based on the experimental results, several co-production schemes were modelled and evaluated with respect to the reference case of bio-SNG production. The economic evaluation revealed that the co-production schemes considered lead to a reduction in the production costs of bioSNG with 5-20% compared to the reference case. Further decrease of the cost can be achieved by e.g. increasing the production scale, going for cheaper biomass feedstock, and/or increasing the yield of target compounds (benzene and ethylene) in the MILENA gasifier. These options will be further addressed in the follow-up Blue Bird project.

1. Introduction

Gasification is a thermochemical process for the conversion of solid or liquid carbonaceous fuels into a combustible gas. Depending on its composition and its degree of cleaning and conditioning, this product gas can be used for a range of different applications, as shown in Figure 1. Since biomass gasification produces a gas with a significant amount of valuable compounds, high-value applications beyond the production of power and heat, e.g. synthesis of biofuels and chemicals, are getting increasing attention.

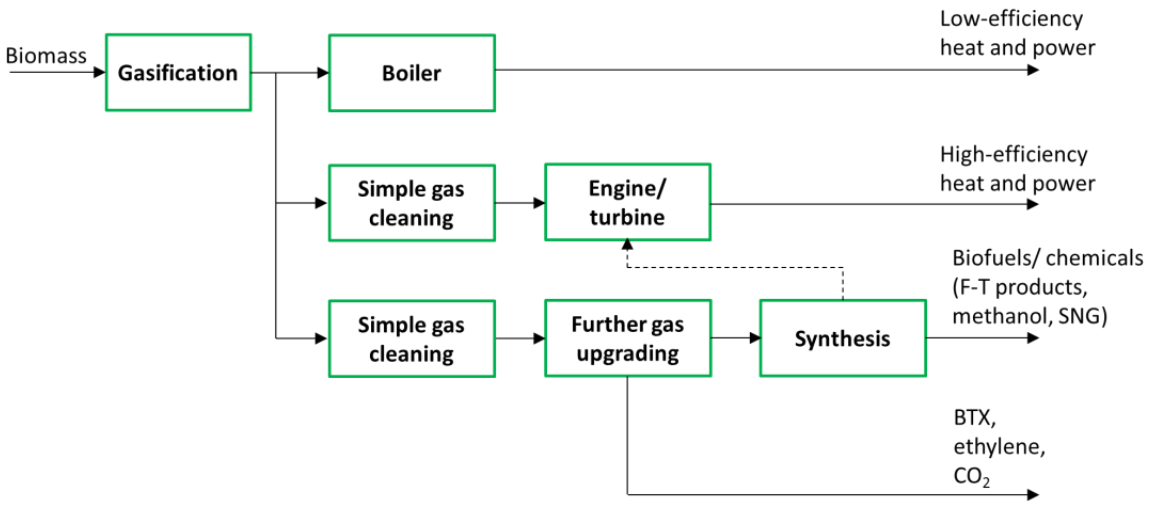


Figure 1. Simplified overview of different applications of producer gas from gasification.

Figure 1 shows that a low-value application like heat production requires minimal gas cleaning, and as the value of the application increases, so does the level of cleaning and upgrading required for the gas. Co-firing of producer gas in a boiler, as in the case of the Amer 9 power plant, is a relatively simple way of converting biomass for the production of heat and power. If the gas is fed to an engine or a turbine, the degree of gas cleaning (dust removal, tar removal) is higher. An example of this type of application is the Güssing plant in Austria, already in operation for several years. In case the producer gas is used as feedstock for biofuel production, additional gas upgrading besides dust and tar removal (e.g. acid gas removal, adjustment of the H_2/CO ratio, compression) is necessary. An example of this type of application is the recently commissioned GoBiGas plant in Sweden, where biomass is converted to Synthetic Natural Gas (SNG) via gasification. In this case, the 'green gas' product offers the advantages of easy storage, existing infrastructure, and social acceptance.

An additional option is the production of green chemicals. This is a relatively new route which is becoming increasingly important. For this, 2 pathways can be identified: the maximization of the production of green chemicals, and the selective removal of green chemicals from the producer

gas. The rest of the gas can be further directed to the final application, either as fuel in an engine/turbine or as feedstock to the synthesis unit, in such a way that the value of the conversion chain is maximized.

With this background, the Green Birds project has focused on the valorisation of chemicals from the producer gas through an innovative route. The main interest of this route for ECN is the co-production of valuable compounds in the green gas process, thus contributing to the decrease of the overall SNG cost. For Avantium, the gasification route is an option for the valorisation of a residue from its YXY process, humins and lignin, besides the production of a green feedstock that can be reused. Green Birds has looked into a number of topics for the development of this novel route. For that, wood but also lignin and humins (which pose a challenge for the feeding to the gasifier) have been considered. The effect of the fuel composition (lignin content) on the production of benzene and ethylene has been studied to determine to what extent the yield of target compounds during the gasification process can be steered. These results are discussed in Chapter 2. The results for the conversion of humins via gasification as a way to valorise this recalcitrant feedstock into green chemicals are analysed in Chapter 3.

Two different separation routes have been analysed. The first one is the production of BTX from producer gas, for which an absorption process has been developed (chapter 3). The second one refers to the separation of ethylene from the gas via adsorption processes (chapter 5). In addition, novel pathways for the reactive conversion of benzene and ethylene to high-value chemicals have been identified and evaluated in terms of technical and economic feasibility. These findings are described in Chapter 4.

2. Effect of gasification feedstock on the yield of BTX and ethylene

2.1 Introduction

The first approach considered in Green Birds for the optimization of co-production schemes is the increase in the yield of high-value compounds (BTX and ethylene) during gasification. For this, it is firstly necessary to understand the mechanisms of formation of target compounds during the gasification process. Based on this first study, different gasification experiments were carried out to determine whether there is a correlation between the lignin content of the gasification fuel and the yield of benzene and ethylene. This section summarizes the main results obtained.

2.2 Formation of benzene during gasification

A literature review carried out at ECN on mechanisms of formation and decomposition of benzene during thermochemical conversion (Ardiyanti, 2014) showed that there are two routes of production of benzene upon pyrolysis, namely the lignin route and the cellulose route. In all cases, benzene is a secondary pyrolysis product, that is, it is produced by reactions between primary pyrolysis products. The benzene formation from lignin comes from deoxygenation of phenol (dominant at 700-800°C) or acetylene cyclic polymerization (dominant at 850-1,000°C). From cellulose, benzene is formed by the reactions between the secondary pyrolysis gases (propylene, butane, dimethyl furan, acetylene). Olefins and BTX are non-equilibrium intermediates and will react further given a prolonged residence time. Benzene can react with another benzene molecule or with acetylene to form polyaromatic cyclic hydrocarbons (PAHs). Polymerization reactions can be prevented by lowering the partial pressures of reagents (benzene, acetylene). From previous tests at ECN, lignin seemed to be the main source of benzene.

Based on the conclusions of this study, some options were suggested in order to control tar formation (i.e. minimize further reactions of benzene), e.g. the possibility of controlling the residence time within the MILENA gasifier, or quenching of the producer gas in order to reduce the gas temperature and to dilute the benzene/olefins.

2.3 Effect of lignin content: gasification tests with DDB and beech wood

Gasification tests were performed at ECN in the MILENA gasifier in 2014 in order to determine the effect of the feedstock composition on the distribution of components of the resulting producer gas in order to maximize the production of high-value compounds (e.g. benzene, ethylene). In particular, the effect of the increase of the lignin content of the biomass feedstock was studied. For this, wheat straw-derived dried distilled biomass (DDB), a lignin-rich low-value feedstock from biorefinery processes, was fed in mixtures with beech wood to determine the effect of the composition of the parent fuels on the producer gas composition. The composition of this fuel is summarized in Table 1.

Table 1 Thermochemical characterization of wheat straw-derived dried distilled biomass (DDB).

Wheat straw DDB		
Biochemical analysis (a.r.)	Unit	Value
Arabinan	%	0.56
Xylan	%	4.49
Galactan	%	0.49
Glucan	%	15.79
Rhamnan	%	0.03
Acid insoluble lignin - ash	%	50.13
Acid soluble lignin	%	2.56
Proximate analysis (a.r.)		
Ash 550°C	%	12.2
Ash 815°C	%	12.0
Moisture (105°C)	%	7.1
Volatile matter	%	63.2
Ultimate analysis (a.r.)		
C	%	50.3
H	%	5.9
N	%	2.0
O	%	31.6
S	mg/kg	3,067
HHV	kJ/kg	20,654
Elemental analysis (d.b.)		
Si	mg/kg	42,000
S	mg/kg	3,067
K	mg/kg	2,925
Ca	mg/kg	2,680
Na	mg/kg	1,584
Al	mg/kg	1,399
Fe	mg/kg	978
P	mg/kg	835

As can be seen in Table 1, DDB contains ~ 50wt.% lignin (as a comparison, the lignin content of beech wood is ~20wt.%), thus it is a good candidate to evaluate the effect of increasing the lignin content of the gasification fuel on the yield of benzene and ethylene.

Table 2 shows an overview of the tests performed with beech wood (BW), dried distilled biomass (DDB), and mixtures thereof.

Table 2 Overview of tests carried out with beech wood (BW) and wheat-straw DDB (DDB).

Description	BW 100	BW 50/DDB 50	DDB 100	DDB 100
Date start	25/02/14	25/02/14	25/02/14	25/02/14
Duration	7:31 – 8:26	8:26 – 9:03	9:16 - 10:59	10:59-13:26
Fuel 1	BW	BW	-	-
Fuel bunker	A	A	-	-
Fuel flow 1(kg/h)	5.1	2.5	-	-
Fuel 2	-	DDB	DDB	DDB
Fuel bunker	-	B	B	B
Fuel flow 2 (kg/h)	-	2.8	5.2	5.2
Bed material	Fresh Austrian olivine			

The detailed results can be found in the note ECN-BEE-2014-180. This chapter will show the main results obtained. Firstly, Figure 2-Figure 5 give an overview of some results obtained in the gasification of wheat derived dried distilled biomass (DDB) and beech wood. Firstly, the trends of gas composition throughout the test, displayed in Figure 2, show that stable operation was achieved throughout the test. In order to evaluate the effect of the feedstock composition, Figure 3 plots the effect of the DDB content in the fuel on the producer gas composition on dry basis. The DDB content, which ranges from 0 wt.% (i.e. only beech wood) to 100 wt.%, is equivalent to a variation in the lignin content from ~20 wt.% to 50 wt.%. The more significant trends correspond to a slight decrease in CO concentration from 35% vol. to 30% vol. (dry basis), an increase of C_6H_6 from 8600 ppmv to 12000 ppmv and a linear increase in the H_2S from 250 ppmv to 2500 ppmv. The ethylene concentration increases slightly from 4.2% vol. to 5.8% vol.

Figure 2 Overview of producer gas composition during experimental testing of beech wood (BW) and wheat straw-derived dried distilled biomass (DDB) measured by online gas analyzer.

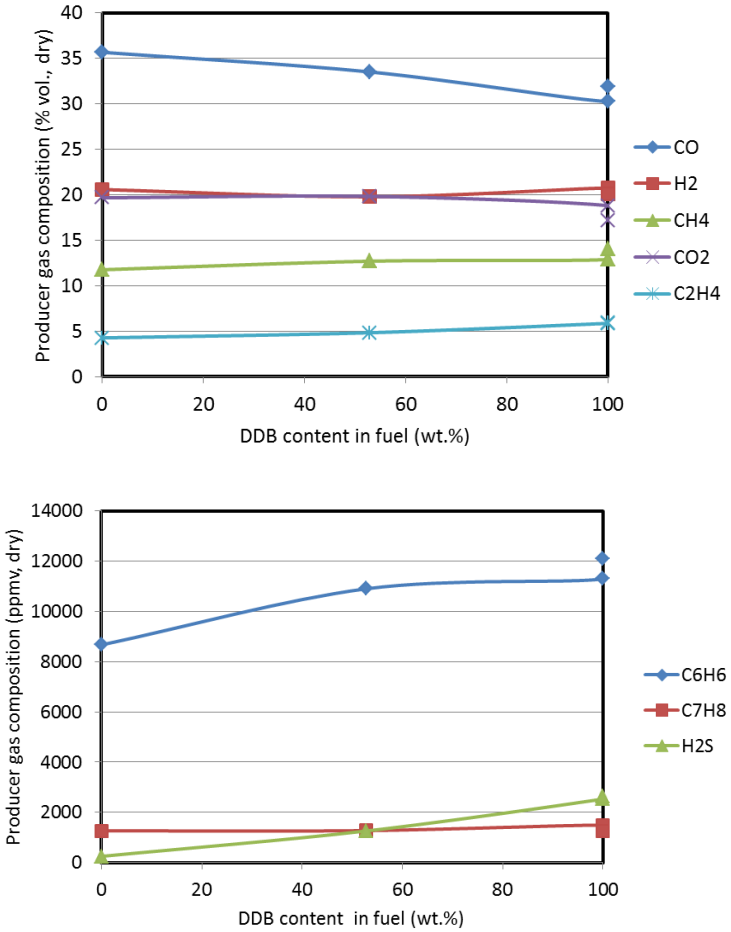


Figure 3 Effect of the content of DDB in the feedstock on the composition of producer gas (dry basis).

The concentrations of the carbonaceous compounds have been converted to yields, expressed in kg compound/kg dry, ash-free basis fuel. The yields take into account not only variations in gas composition, but also changes in carbon conversion, and are therefore a valuable parameter to get better insight on the effect of lignin on the production of target compounds (BTX and ethylene). From molar balances performed in the tests, it was found that carbon conversion decreased from ~70 wt.% to 50 wt.% when increasing the DDB content from 0% to 100%. This is a logical trend, since lignin is less reactive than cellulose and hemicellulose and tends to leave the riser as unconverted char which is afterwards burned in the combustor side. The yields are plotted in Figure 4. As can be observed, the only compounds that show a significant variation are CO and ethylene. CO decreases linearly from 0.35 to 0.25 kg/kg in the range of compositions tested. Ethylene yield increases from 0.04 to 0.05 kg/kg, but this trend occurs only when increasing the DDB fraction beyond 50 wt.%. The yield of the rest of carbonaceous compounds remains approximately constant throughout the range of fuel compositions tested.

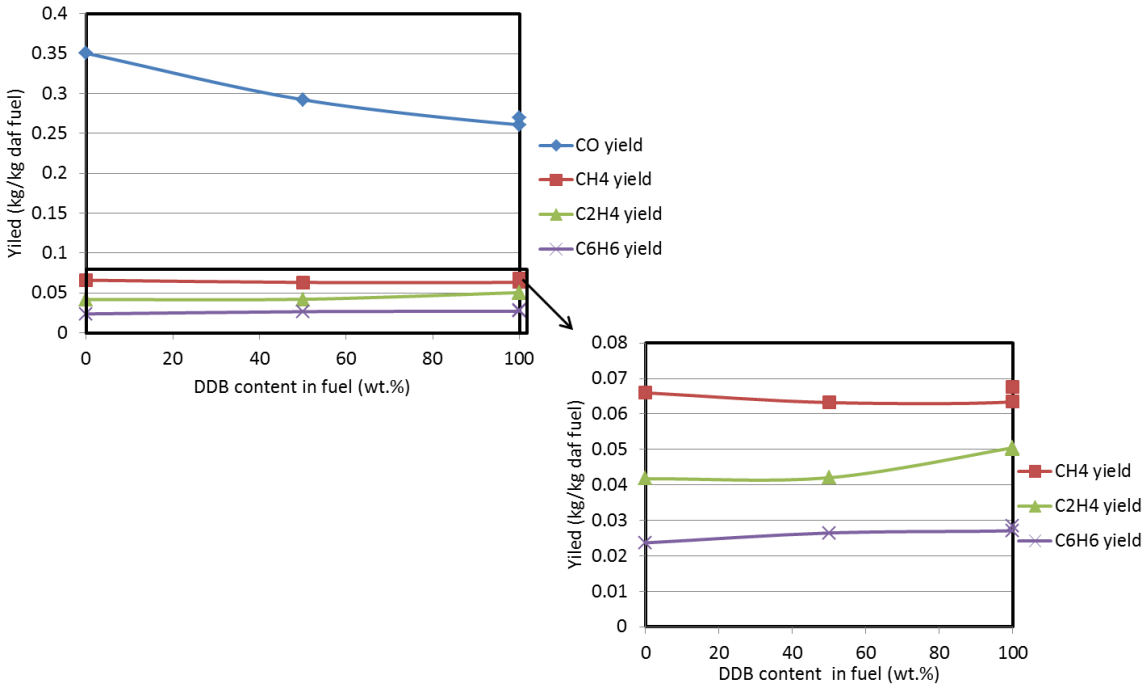


Figure 4 Effect of the content of DDB in the feedstock on the yield (kg/kg dry, ash-free fuel) of carbonaceous compounds.

Lastly, Figure 5 shows the results of tar content and composition measured for the parent fuels and the mixture of beech wood and DDB. The tar groups follow ECN's tar classification, where class 4 and class 5 correspond to heavy tars. The addition of DDB to the fuel mixture leads to an increase in tar content from 30-35 g/Nm^3 to ~ 50 g/Nm^3. The lignin content influences class 4, class 5 and the unknown fraction of tars. However, it is interesting to observe a non-linear behavior in the tar production, with minor differences between the mixture 50 DDB/50 BW and the pure DDB.

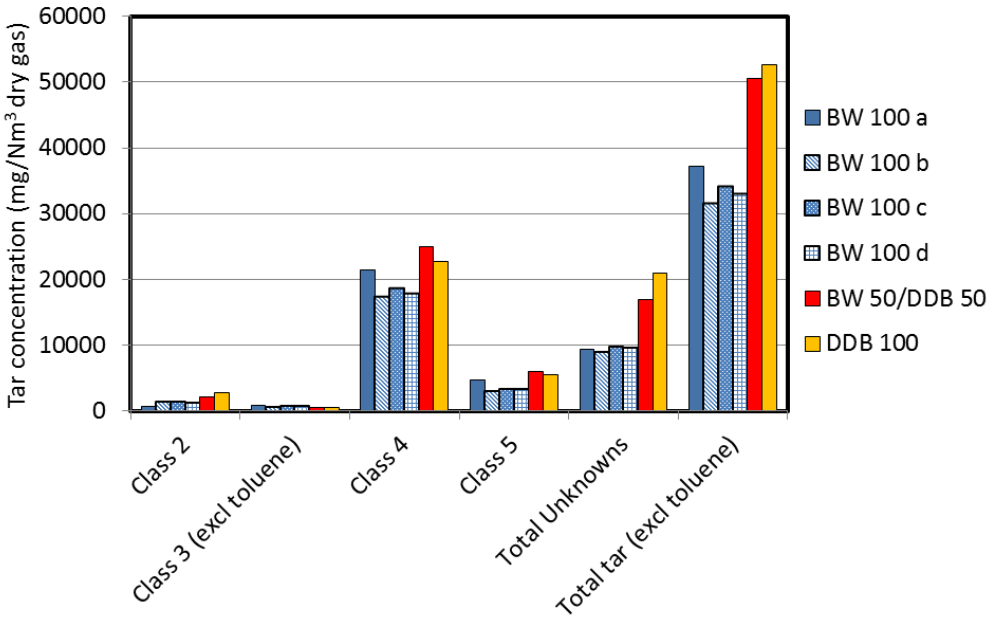


Figure 5 Effect of the content of DDB in the feedstock on the content and composition of tar compounds (see ECN tar classification in http://www.thersites.nl/). The different blue bars correspond to SPA results of MILENA operating with beech wood (BW 100) at similar operating conditions as the tests with DDB.

3. Conversion of humins

3.1 Introduction

The Avantium YXY process converts carbohydrates into various furanic compounds which can subsequently be used as building blocks for the production of polymers and biofuels. The acid-catalyzed conversion of the (hemi-)cellulose fraction of lignocellulosic biomass to furanics is, however, unavoidably accompanied by the formation of humin by-products. Humins are carbonaceous, heterogeneous, polydisperse materials whose molecular structure is largely unknown. Humin has the appearance of syrup with a high viscosity at room temperature, and it can be considered, just as lignin, as a recalcitrant feedstock that needs to be valorized in order to increase the competitiveness of biorefinery processes.

Currently there are no conversion routes for this residual stream due to the challenges it poses, particularly its feeding and its behaviour during heating up. Within Green Birds, conversion of humins via combustion and gasification has been studied. Moreover, conversion of wood and lignin and mixtures thereof has also been analysed with focus on the yields of BTX and ethylene. The results of the experiments performed are described in this chapter.

3.2 Characterization of humins

Prior to the study of the performance of humins in combustion and gasification processes, a characterization of the feedstock was performed in order to allow for a proper design of the feeding system and the identification of appropriate gasification operating conditions. A detailed description of the characterization measurements performed can be found in the documents ECN-BEE-2014-349 and ECN-BEE-2015-018. The properties of the humins are summarized in Table 3.

Moreover, a thermogravimetric analysis (TGA) was performed (heating up from 20°C to 800°C at a rate of 2°C/min). However, the measurement was not successful due to the boiling/expansion of the material inside the oven at 140-160°C. The inspection of the sample after the test revealed that it probably swelled out of the cup and exploded at about 160^{o}C.

Table 3 Characterization of humins.

Property	Value
Density (kg/m^3)	~ 1250
Viscosity	4000-5000 mPa·s at 20^{o}C 50-100mPa·s at 100^{o}C
Moisture content (wt.%, as received)	3
Heating value (MJ/kg, dry basis)	23
Ultimate analysis (wt.%, dry basis)	
C	57
H	5.7
O	37
N	<0.1
Ultimate analysis (mg/kg, dry basis)	
Cl	24
S	1101
Al	1.8
K	16
Na	14867

3.3 Combustion of humins

A great challenge associated to the conversion of humins relates to its feeding to the reactor. Below 80°C, this syrup-like feedstock is too viscous, but above 100°C there are issues of foam formation. Within this project, a feeding system was developed, constructed and optimized so that liquid humins can be atomized and combusted. The feeding system is composed of a heated storage vessel with a pump for the atomization of the liquid humins in a drop tube reactor. The combustion of humins was eventually successful by sufficient atomization of the fuel. However, deposits occurred due to the high concentration of sodium in the material.

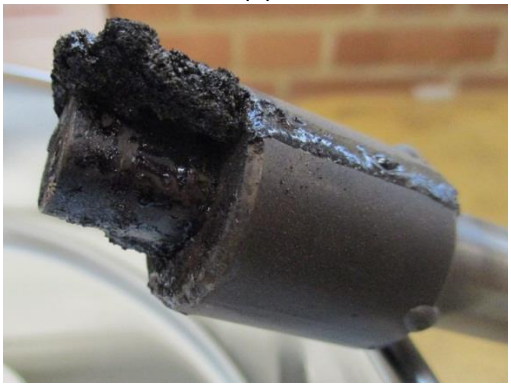
3.4 Gasification of humins

The principle for the conversion of humins via gasification is similar as that considered for combustion. However, the feeding system had to be adapted due to the different feeding rates used in the gasification and combustion setups. For this, a higher-capacity pump was implemented. The feeding system can be observed in Figure 6.

Figure 6 Setup for feeding of humins to the MILENA gasifier.

Although the feeding of humins to the MILENA gasifier was successful, problems arose within the reactor. The humins produced a kind of foam with a very low reactivity, which led to the formation of chunks. These pieces in turn caused the blockage of the internal circulation of bed material between the combustor and the riser zones. This can be observed in Figure 7.

(a)



(b)

(c)

Figure 7 Operational challenges of humins gasification: blockage found in the riser of MILENA gasifier (a); foaming and plugging of feeding nozzle (b); blockage in bottom part of MILENA riser and recirculation hole (c).

The feeding of large droplets and the high feed flow in the facility (~ 4 kg/h) led to operational issues related to the formation of foam. For this reason, it was decided to implement the nozzle that was used in the combustion experiments. This nozzle produces very small droplets which minimize the formation of foam. During this second experiment, it was possible to operate for a longer time, but another problem appeared. The nozzle was vertically implemented, approximately 10 cm below the hole of sand supply. This had the disadvantage that the bed

started earlier to agglomerate before the complete decomposition of the humin. In a second try, the nozzle was higher positioned, just below the hole of sand supply. This experiment went better, but even so blockages occurred.

To sum up, the gasification of humins at lab-scale proved challenging, but not unfeasible. Lessons learned from the experiments show that it is preferable to use mechanic feeding systems using a pump rather than pneumatic. Pump feeding leads to a more constant flow. Moreover, it is important that the humins feedstock is well atomized and directly entrained with the hot bed material. At small scale this was a limitation. On the other hand, due to the high concentration of sodium in the fuel, which eventually leads to problems of deposits, corrosion and agglomeration, it would be necessary to use a "getter" material (e.g. dolomite, aluminosilicate materials) in the bed in order to bind the sodium to less troublesome compounds.

3.5 Improving feeding issues of humins/lignin by mixing

3.5.1 Mixing humins and wood

Preliminary tests showed that the foaming effect of humins does not appear when put on a porous carrier. Wood chips possess this porosity up to a certain extent, thus an alternative strategy for the conversion of humins is the feeding of mixtures of humins and beech wood. For this purpose, a mixture of 25 wt.% humin in beech wood was prepared for gasification testing. Wood was impregnated by dissolving humins in acetone and evaporating acetone. The progress of the test can be observed in Figure 8. The experiment started with beech wood. Once stable conditions were reached, the mixture was started to be fed at 54 Hz, but the feeding frequency was reduced since the flow of humin-impregnated wood was higher. An interesting fact was that the feeding of the mixture led to a shift between H_2, CO and CO_2. This is probably a consequence of the high content of sodium present in the fuel, which might act as a catalyst for the WGS reaction. Little change was observed in the concentration of benzene, but the concentration of H_2S did increase significantly from 200 ppmv to ~ 450 ppmv, and the ethylene content decreased from ~4 vol.% to approximately 3 vol.%.

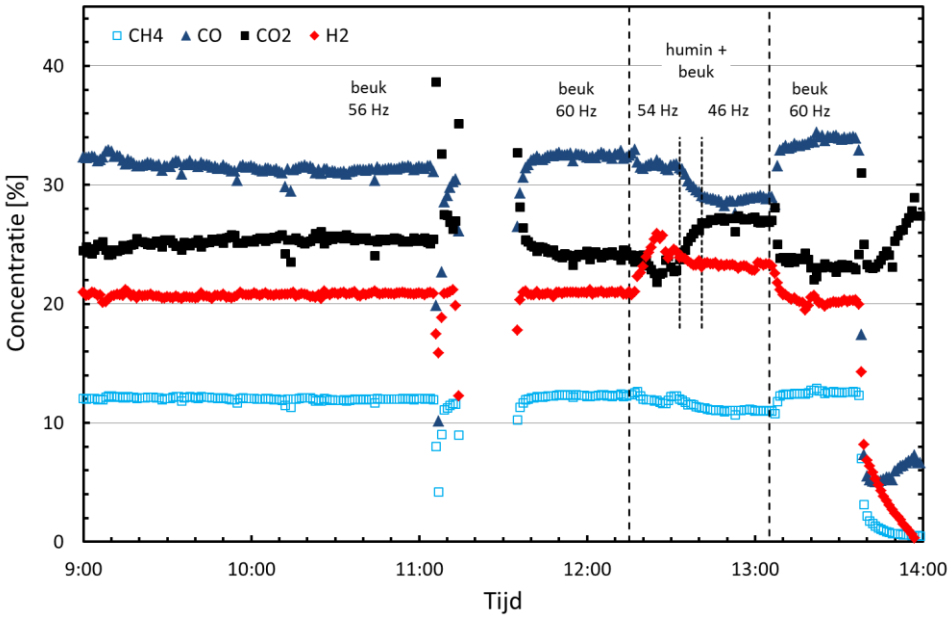


Figure 8 Gasification test using a mixture of 25wt% humin on beech wood chips: concentration of CO, CO_2, H_2 and CH_4 (dry basis) in producer gas.

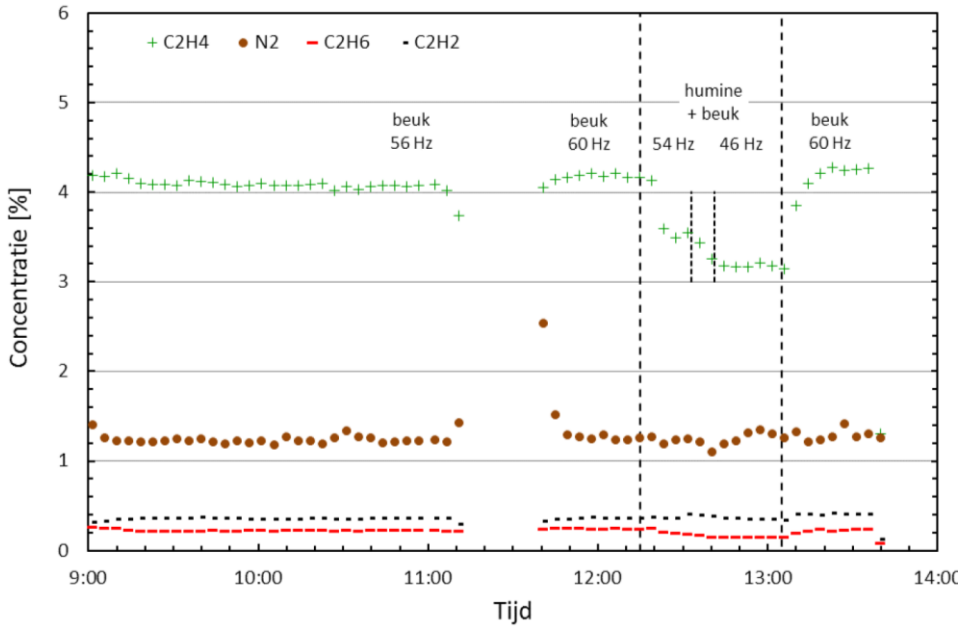


Figure 9 Gasification test using a mixture of 25wt% humin on beech wood chips: concentration of N_2, ethane, ethylene and acetylene (dry basis) in producer gas.

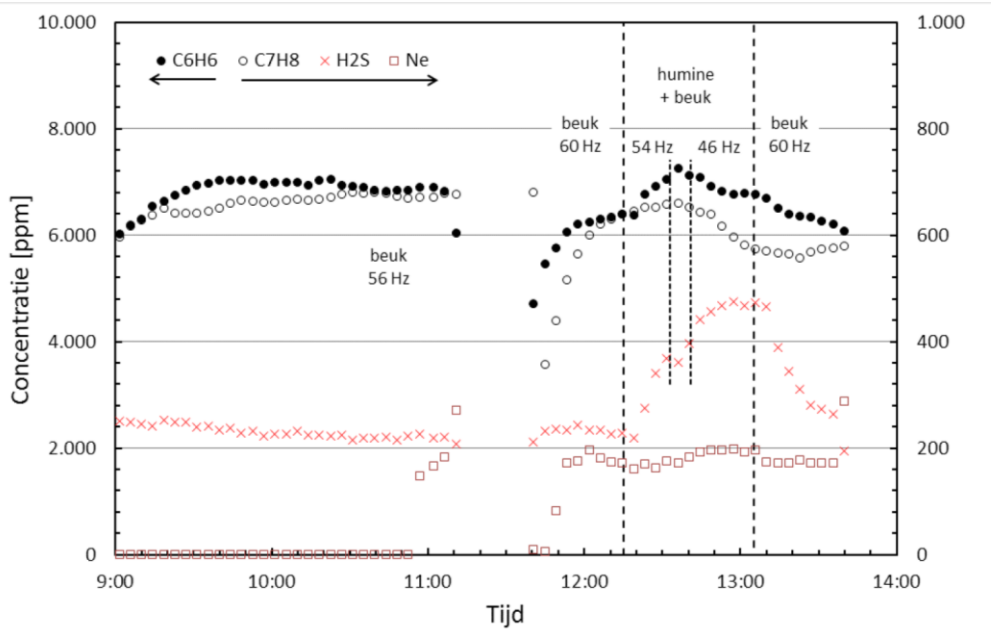


Figure 10 Gasification test using a mixture of 25wt% humin on beech wood chips: concentration of Ne (tracer gas), benzene, toluene and H_2S (dry basis) in producer gas.

3.5.2 Mixing humins/lignin and clay

Following the same principle of loading the troublesome foam-forming materials (humins or lignin) into porous carriers in order to reduce the expansion/explosion behavior of these materials when heating up, additional oven tests were performed by mixing lignin and humin with a high-porous natural clay (sepiolite) in different ratios (30%, 50%, and 70wt.%) in order to investigate its melting/foaming behavior.

Mixture	Result, 500°C for 20 minutes	
Lignin:clay 1:1	Turned black, charred and remained in powder form.	
Humin:clay 1:1		
Lignin pure	Bubbled /exploded/agglomerated	
Humin pure		

Figure 11 Oven tests using mixtures of clay and humins/lignin: comparison of behavior of mixtures and pure humin/lignin.

The feeding mixtures were prepared by mixing the lignin/humin, the clay and water to form a paste, drying of the mixture, and crushing to particle sizes of 0.5-5 mm. These mixtures were introduced to an oven at 2 different temperatures (350°C and 500°C).

Some examples of the results can be found in Figure 11. Unlike the pure samples of lignin and humin (which showed bubbling, explosion and agglomeration upon heating up), the mixtures of lignin/humin + clay remained in its original state. These preliminary tests showed that the addition of clay is another feasible way to overcome the feeding problems associated to lignin-based feedstock. A content of 30% wt. clay in the feeding is sufficient to effectively feed lignin and humin into a thermal process.

3.5.3 Conclusions

From the test performed it appears that impregnating humins in a porous carrier (e.g. wood, clay) is a feasible alternative in order to properly feed humins into a gasifier or a combustor. The gasification tests performed allowed gathering valuable information about the humin gasification process. However, further work would be required for the optimization of this strategy. Moreover, it might be worth exploring in future work alternative solutions, such as improvements in reactor design to cope with troublesome feeds (e.g. variable fuel feed rate, 2-step gasification, etc.).

4. Recovery of BTX from producer gas

4.1 Introduction

Benzene is an important compound in producer gas from medium-temperature gasification. Depending on the operating conditions, producer gas can contain 0.5-1 vol.% benzene. However, 1 vol.% benzene means 10% of the energy contained in the gas, which is a significant amount. Depending on the gasification feedstock, the benzene concentration can increase up to 2.5 vol.%. Besides benzene, also toluene is produced, but the yield of toluene is one order of magnitude lower than that of benzene. Xylenes are also produced in low concentrations.

The capture of BTX (benzene, toluene and xylenes) is a promising option for the co-production of energy/biofuels and green chemicals. Given the high added value of BTX, their recovery is an interesting alternative to reduce the production cost of biofuels such as SNG.

With this background, this chapter reports the results of BTX capture performed in the framework of the Green Birds project.

4.2 Sorbent selection

In a previous work (ECN-X—13-076), several sorbents had been screened for BTX capture from producer gas. In this work, other processes were considered, such as membranes and cryogenic separation, in order to separate BTX from producer gas. Membranes posed a problem of selectivity and thus on the size of the membrane unit, and the use of cryogenic separation requires the prior deep removal of CO_2 and H_2O in order to avoid operational problems in the cold box. In addition, the energy consumption of the cryogenic unit is very high. Other existing processes are suitable for other gas compositions and concentrations, but cannot be directly applied to gasification producer gas. Eventually, it was decided to use a liquid absorption medium, partly because ECN had already gathered significant experience in this field from the development of the OLGA tar removal system. In addition, a number of requirements can be placed on the liquid in terms of composition, vapor pressure, thermal- and chemical stability, viscosity, etc. From this, Triclosan, a simple molecule, was at first selected. However, after some tests it was decided to select a different liquid sorbent. The solidification temperature was a critical factor influencing the fall of Triclosan as a suitable sorption liquid.

Another commercial silicon-based oil was used as sorbent in further experiments. The properties of this compound make it ideal for efficient removal of BTX. This is described elsewhere (ECN-X—15-048). Particularly the thermal and chemical stability of this sorbent is extremely good as well as a relatively low vapor pressure at high temperature with respect to other sorbent liquids.

4.3 Absorption and stripping with nitrogen

The first tests were carried out in a setup where absorption and stripping could be carried out, but where no additional action was performed on the gas from the stripper. These preliminary experiments with the liquid were performed in 2014, where nitrogen was used as stripping gas. In Figure 12 it can be seen that the absorber captures the inlet benzene at 40°C. The inlet concentration of benzene in producer gas is between 7000 ppmv and 8000 ppmv. The outlet concentration when nitrogen is used as stripping gas is 400-500 ppmv. Thus, the benzene removal during this first experiment was above 90%.

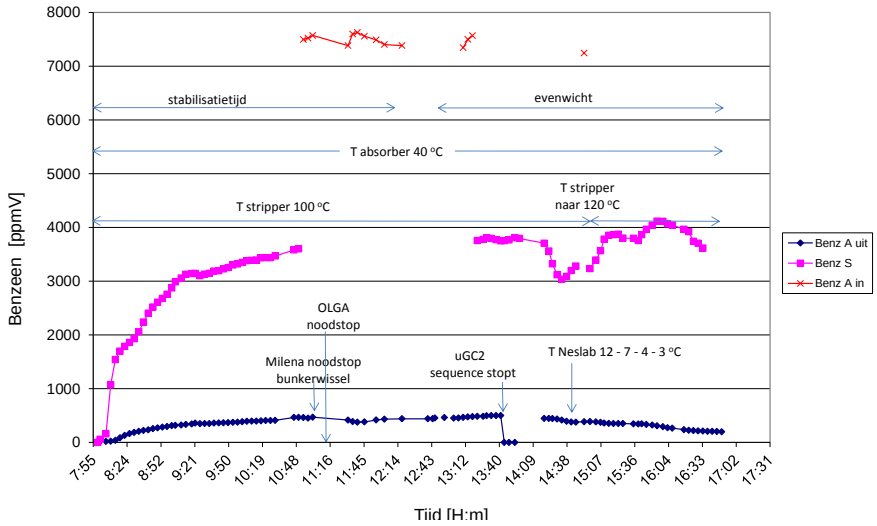


Figure 12 Overview of test 1 performed on 02-04-2014 – absorption of BTX using nitrogen as stripping medium.

4.4 Absorption and stripping with steam

The encouraging results of BTX removal with nitrogen as stripping medium led to the following step, namely the use of steam in the stripper for the further recovery of the removed bio-BTX by condensation as a product. For this, the ECN model developed for the prediction of the process efficiency was firstly adapted in order to select the operating conditions for the implementation of steam stripping in the lab-scale.

Figure 13 shows the comparison of the modelled system efficiency using nitrogen and steam as stripping fluid. As can be seen, at a similar temperature and 1 Nm^3/h stripping, the removal efficiency with nitrogen is 98%, and it is reduced to 94% when replacing nitrogen with steam.

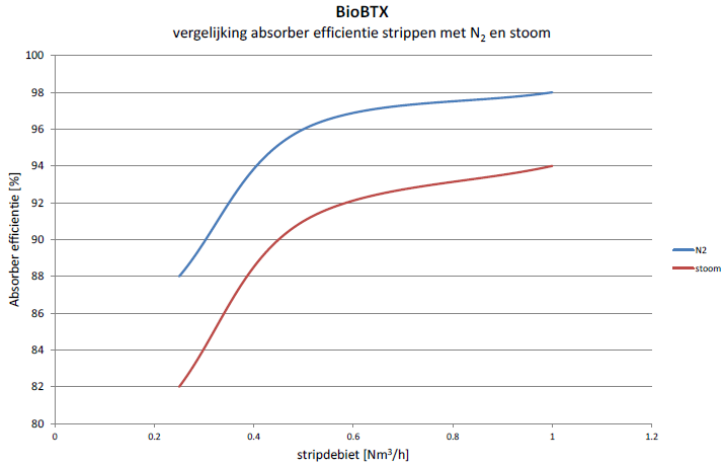


Figure 13 Comparison of BTX removal efficiency using steam (red line) or N_2 (blue line) as stripping medium (calculated values from model).

Based on the model results, an experimental plan was designed to prove the BTX removal concept at lab scale. An important milestone for bio-BTX recovery was reached in November 2014, where > 1 kg BTX was harvested for the first time from biomass gasification producer gas at ECN laboratories. Figure 14 shows the experimental facility for BTX scrubbing from producer gas. The results of this test are described in the note ECN-BEE-2015-024. During the test, the effect of the stripping steam flow on the performance of the BTX unit was determined. A BTX removal of ~94% was achieved. The recovered bio-BTX can be seen in Figure 15 and Figure 16. During the test, circa 14 NL/min producer gas was fed to the BTX scrubber for almost 76 hours. The absorber operated at 35°C. The addition of a tracer gas and the online measurement of the inlet and outlet gas compositions allowed the performance of mass balances and the calculation of the removal efficiency.

Figure 14 BTX scrubber setup at ECN laboratories.

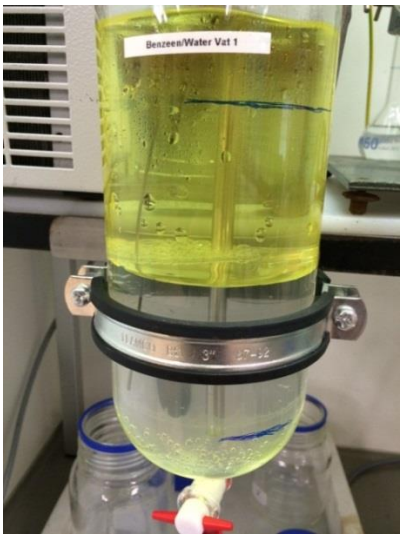


Figure 15 Bio-BTX recovery during tests in November 2014. The upper yellow layer corresponds to bio-BTX, the lower layer is condensed water from the stripper.

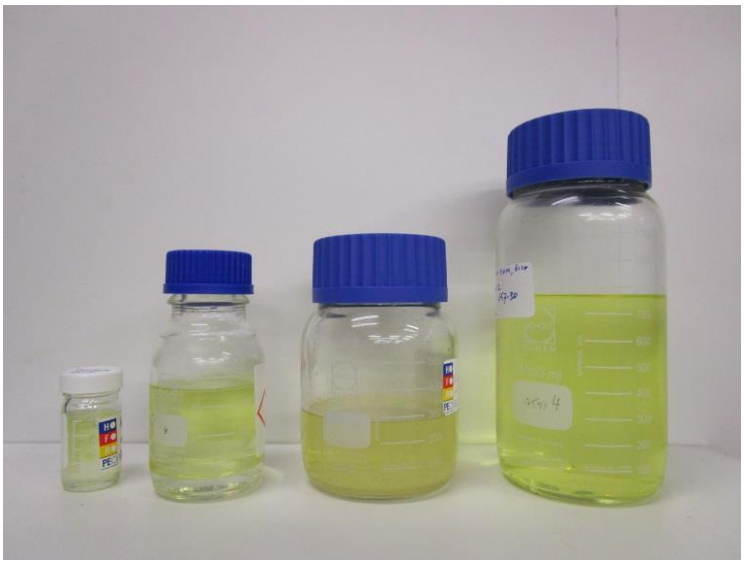


Figure 16 Total bio-BTX harvest during test in November 2014.

Table 4 Composition of the bio-BTX, test November 2014.

Total bio-BTX (g)	1,091.36
Bio-BTX composition (wt.%)	
Benzene	86.6
Toluene	6.54
Xylenes	0.2
Total BTX	**93.34**
Ethylbenzene	0.15
Styrene	1.14
Cresol	0.28
Naphthalene	0.57
Rest aromatics + unknowns	0.72
Thiophenes	0.12

An overview of the performance of BTX removal can be observed in Figure 17. As can be seen, the removal efficiency kept around 94% when operating the stripper with 820 g/h. On the 14th November, the effect of the steam flow on the performance of the unit was evaluated. Reducing the stripping steam to ¼ of the initial flow made the efficiency drop to 82%. Although the unit was continuously in operation, the lack of data from micro-GC (outlet gas composition) was responsible for blank periods where the efficiency could not be evaluated.

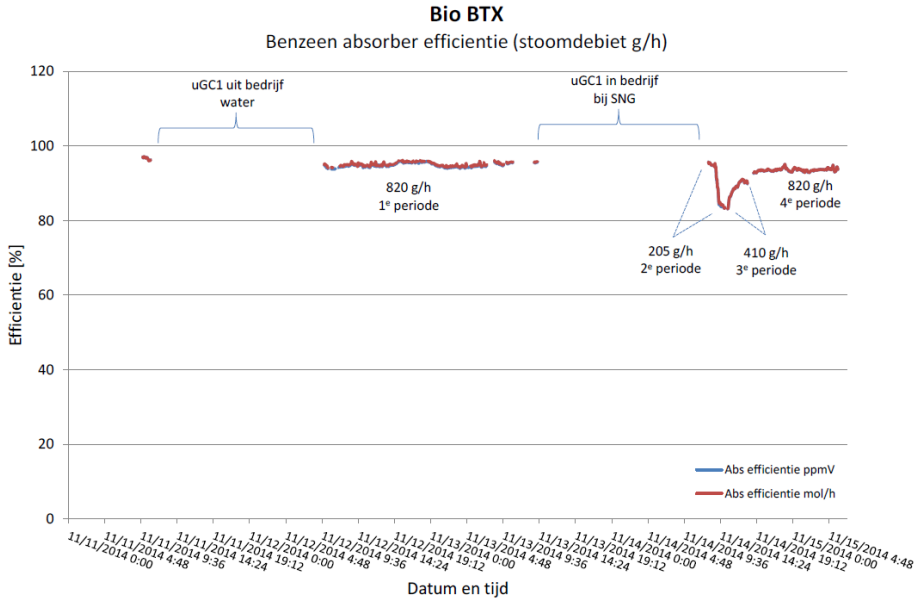


Figure 17 Removal efficiency of the bio-BTX absorber during the test in November 2014.

5. Pathways for reactive separation of BTX and ethylene from producer gas

5.1 Introduction

Ethylene and benzene make only a small part of the total volume of producer gas (~ 5% vol.), but in terms of energy, they contribute to a significant extent (~25% energy content). These compounds not only have a detrimental effect on the methanation catalysts in an SNG production process, but they have also a higher economic value than the main product, SNG. Thus, the separation and recovery of benzene and ethylene from producer gas is a promising option that opens the way for the co-production of fuels and green chemicals from biomass gasification by reducing the production cost of biofuels.

During work performed at ECN (V. Krzelj, 2014), a screening of processes for the separation of benzene and ethylene was performed. Cryogenic separation is the only physical process that can allow sufficient level of separation, but the associated costs and energy consumption are very high. A second route is reactive separation, which transforms ethylene into products that are easier to separate and add extra economic value. From this screening process, ethylbenzene production and aromatization of ethylene were identified as the most promising pathways for the combined separation and valorisation of benzene and ethylene from producer gas based on criteria of added value, capital and operating costs, and process integration.

These promising pathways were experimentally tested for a proof-of-concept. This section shows the main results from this work.

5.2 Experimental results

5.2.1 Experimental setup

Two samples of zeolite ZSM-5 were used as catalyst:

- CBV 3014E CY (Si/Al ratio 15, 1.6 mm extrusions with 20 % binder).
- CBV 8014 CY (Si/Al ratio 40, 1.6 mm extrusions with 20 % binder).

Different experiments were performed varying the composition of the inlet feed (actual ethylene/benzene ratio in producer gas and addition of external benzene). The experiments were performed in a fixed-bed tubular reactor placed downstream the MILENA gasifier and the OLGA tar removal system. The inlet and outlet gas composition was measured by online micro-GC analysis, offline GC analysis of hydrocarbons and S compounds, and SPA analysis for the content

and composition of higher aromatics. The operating conditions were: temperature 360-450°C, atmospheric pressure, WHSV = 3 h^{-1}.

5.2.2 Effect of temperature

Figure 18 shows the conversion of ethylene during the first experimental run performed at 2 different temperatures: 360°C and 420°C. The initial conversion of 95% progressively decreased over time up to 81%. At 360°C there was no significant change in benzene concentration over the reactor. It was concluded that at 360°C, reaction rate of benzene production from ethylene aromatization and reaction rate of benzene alkylation to ethylbenzene are equal. At higher temperature, benzene is also being produced, thus the product distribution is shifted towards lower aromatics.

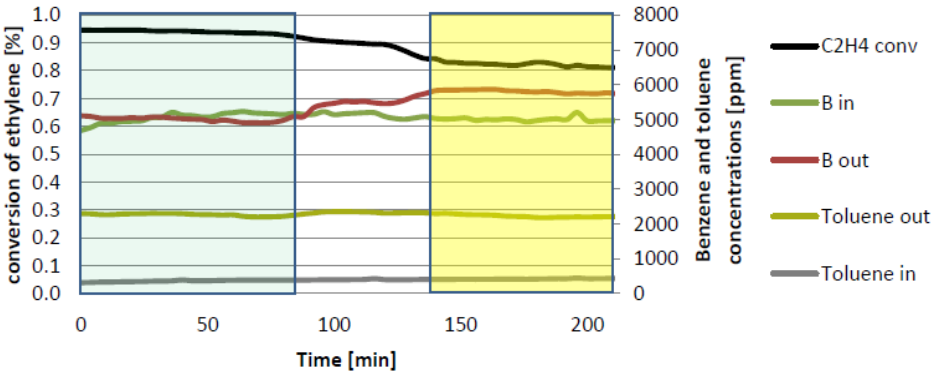


Figure 18 Ethylene conversion and inlet and outlet concentrations of benzene and toluene during benzene alkylation test. Green zone: 360°C; yellow zone: 420°C.

5.2.3 Effect of benzene concentration

A small increase of benzene from 0.5% to 1.1% vol. significantly increases the aromatic distribution towards ethyl-benzene and diethylbenzene. The conversion of ethylene was 87%, of which product distribution towards aromatics was 37%.

5.2.4 Effect of catalyst acidity

A zeolite with a higher Si/Al ratio (Si/Al = 40) was tested to assess the effect of the acidity of the zeolite catalyst. It was found that both the initial conversion (45% compared to 95%) as well as the conversion under stable conditions (20% compared to 81%) were lower with respect to the test with the zeolite with Si/Al = 15. This was expected, since higher Si/Al ratios imply lower acid site density, and thus lower activity.

5.3 Synthesis of ethylbenzene from benzene

The production of polystyrene from bio-BTX and ethylene was also studied within Green Birds. For this, the synthesis of ethylbenzene from benzene and the synthesis of styrene from ethylbenzene were investigated. The objective was to identify suitable green chemistry routes in order to produce a bio-polystyrene product in order to demonstrate the possibility for replacing fossil fuel based polystyrene.

In practise the production of polystyrene in small quantities appeared less simple as expected due to this small scale of the synthesis and because of safety and health constraints with respect to working with benzene. Also the synthesis process at small scale is not necessarily identical to the production process at commercial scale. A number of different synthesis routes for each step in the process are available.

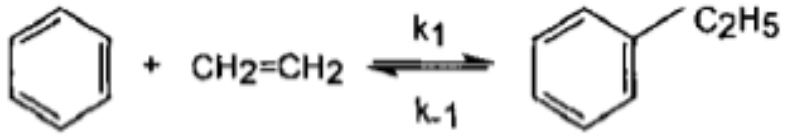


Figure 19 Alkylation of benzene to produce ethylbenzene.

CS Aspa (spin-off company of the University of Groningen) performed a desk study for the synthesis of ethylbenzene from benzene and ethylene via alkylation (Figure 19). This preliminary literature review indicated that the liquid-phase route using a zeolite catalyst (ZSM-5) is more attractive for the 'green synthesis' of ethylbenzene from benzene. There is a dilemma between selectivity and conversion in the first step of the reaction. High pressures (> 20 bar) and low temperatures (< 500 K), are necessary to achieve high conversion. An excess of benzene (4:1 – 5:1 benzene:ethylene) improves the selectivity. The use of zeolites as catalysts and high benzene concentrations (including large recycling stream) contribute to prevent the formation of impurities (e.g. diethylbenzene) in the product.

Further work was carried out at the Avans Hogeschool showed that the production of styrene from ethylbenzene using a bromation and elimination process can be performed in a simple and fast way. Emulsion polymerization is the most optimal polymerization process in terms of simplicity, speed, and high yields.

5.4 Economic analysis of co-production schemes

Based on the results from the experimental tests, several novel co-production schemes were modelled in ASPEN and evaluated with respect to the reference case of bio-SNG production. The co-production cases considered were:

- BTX removal case.
- EB case: Ethylbenzene production process.
- DEA case: Diluted ethylene aromatization process (DEA-1: Conversion of ethylene and distribution of the products obtained from the lab experiments; DEA-2: conversion of ethylene selectivity to aromatics products obtained from literature).

More details over the configuration can be found elsewhere (Krzelj, 2014). The results of the economic evaluation are summarized in Figure 20. As can be seen, all the co-production schemes considered offer a reduction in production costs of bioSNG, with a potential reduction in production cost by 5-20%.

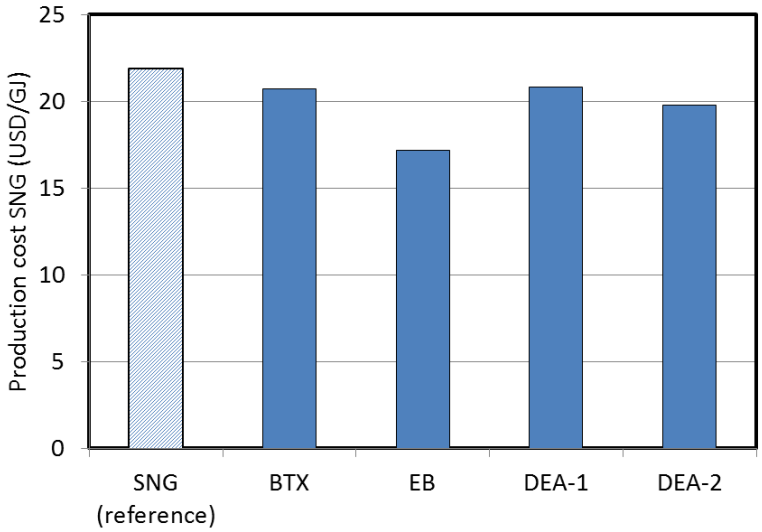


Figure 20 Summary of economic evaluation of co-production schemes: production cost of bio-SNG.

5.5 Conclusions

The experiments performed to prove the feasibility of promising pathways based on reactive separation for the conversion and valorisation of benzene and ethylene from producer gas showed the feasibility of the implementation of reactive separation. High ethylene conversion >90% are achievable, whereas ~40% ethylene was converted to aromatics. The distribution of aromatics was influenced by temperature and addition of benzene to the process. Higher temperatures favour the production of lighter aromatics, whereas higher concentration of benzene at the inlet shifts the product distribution towards ethylbenzene. Two possible strategies are possible: a) developing catalysts with high selectivity towards aromatics and optimizing the reactor conditions to increase selectivity towards one product, and b) feeding additional benzene to the system to increase the selectivity towards ethylbenzene.

The economic evaluation has revealed that the implementation of co-production schemes in the bio-SNG process can reduce the production cost of SNG, even if low prices are assumed for the co-products. The co-production routes considered in this study can reduce the production cost of bio-SNG with 5-20%. Other options to achieve further decrease of the cost include increasing the production scale, going for cheaper biomass feedstock, and/or increasing the yield of target compounds (benzene and ethylene) in the MILENA gasifier.

6. Separation of ethylene from producer gas

6.1 Introduction

In previous chapters, the formation of benzene during thermochemical conversion and its recovery from producer gas have been analysed. Besides benzene, producer gas also contains a significant concentration of ethylene, another valuable bulk chemical. WP.4 of the Green Birds project has focused on the separation of ethylene from producer gas. The separation process considered within the project has been adsorption. For that, work has been carried out for the development and testing of suitable sorbents. This chapter reports the main results obtained. Details can be found elsewhere (Avantium internal report).

6.2 Selection of sorbent for ethylene separation

Avantium has extensively worked on the development of a process for the separation of ethylene from producer gas. For this, the first step is the synthesis of suitable sorbents. Zeolites were investigated for their good adsorption properties. A preliminary screening of different commercial zeolites showed that low Si/Al types, such as X and A, were good ethylene sorbents.

The selected X and A zeolites were then functionalized by e.g. ion exchange or organic modification, in order to tune their selectivity for ethylene. Zeolite A was exchanged with different alkali, alkali earth and transition metals. Adsorption tests with commercial [K]A, [Na]A and [Ca]A demonstrated the effect of pore size on adsorption. An example of these tests is shown in Figure 21. The pores of [K]A were found to be too small to adsorb any of the studied compounds, while [Na]A adsorbs ethylene but the adsorption is kinetically limited (weak adsorption). On the contrary, [Ca]A can adsorb ethylene without kinetic limitation. The adsorption capacity of [Ca]A increases with increasing pressure and decreasing temperatures. Among the functional zeolites tested, the largest ethylene adsorption capacities were found for zeolite [Ca]A and [Ag]A, with up to 7wt% ethylene adsorbed at 40 °C and 5 bar. An example of performance of the [Ca]A material in a complex gas feed is plotted in Figure 22.

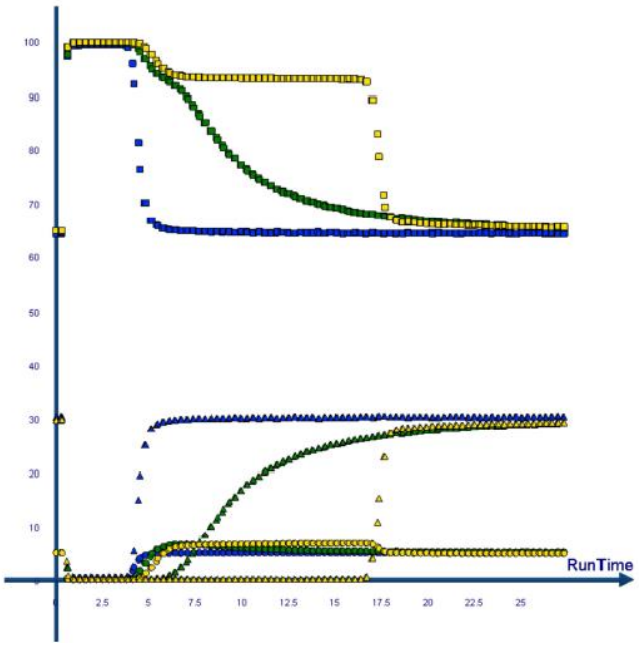


Figure 21 Adsorption curves of ethylene by different A zeolites for the effect of pore size: [K]A (blue), [Na]A (green) and [Ca]A (yellow). Conditions: 100°C, 5 bar, 2 mL/min feed. Y axis represents gas concentration measured by mass spectrometry. Feed mixture: 65% vol. N_2 (squares), 30% vol. ethylene (triangles), 5% vol. Ar (circles).

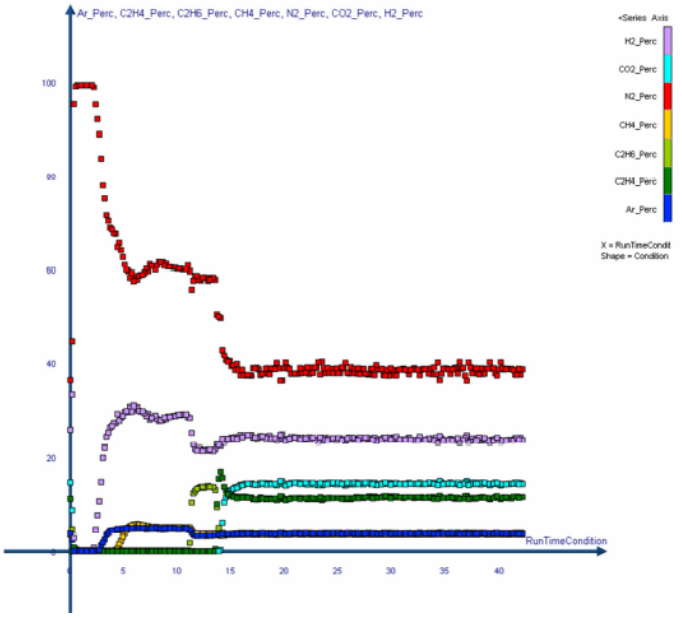


Figure 22 Adsorption of different gases on [Ca]A zeolite at 40°C, 5 bar, and 3 mL/min complex feed mixture (65% vol. N_2, 15 vol.% ethylene, 5 vol.% ethane, 5 vol.% CH_4, 5 vol.% CO and 5 vol.% Ar) mixed with 0.5 mL/min H_2 and 0.5 mL/min CO_2. The signals of CO and N_2 are added up due to spectral overlap (CO was not adsorbed).

It was found that ethylene did not adsorb on wet [Ca]A, which indicates that the adsorption will be affected by the presence of H_2O in the producer gas. This implies that water removal would be necessary prior the adsorption unit. On the contrary, [Ag]A showed good adsorption of ethylene on the wet zeolite. Another limitation of [Ca]A is that ethane and CO_2 were co-adsorbed by the material (Figure 22). The co-adsorption of CO_2 could limit the adsorption of ethylene when working with a CO_2 rich gas mixture, as is the case of producer gas. In comparison, [Ag]A was able to selectively adsorb ethylene in the presence of CH_4, C_2H_6, CO, CO_2 and H_2. However, desorption

experiments with [Ag]A indicated that ethylene was more difficult recovered than from [Ca]A. A regeneration/desorption step at 200 °C is needed to recover 80% of the original ethylene adsorption capacity of [Ag]A. This is probably caused by reduction of the silver oxides to metallic silver. Long-term stability tests (Figure 23) showed a decrease in ethylene adsorption selectivity and capacity of [Ag]A over 15 adsorption/desorption cycles On the contrary, [Ca]A was a very stable sorbent with a constant adsorption capacity over several adsorption/desorption cycles.

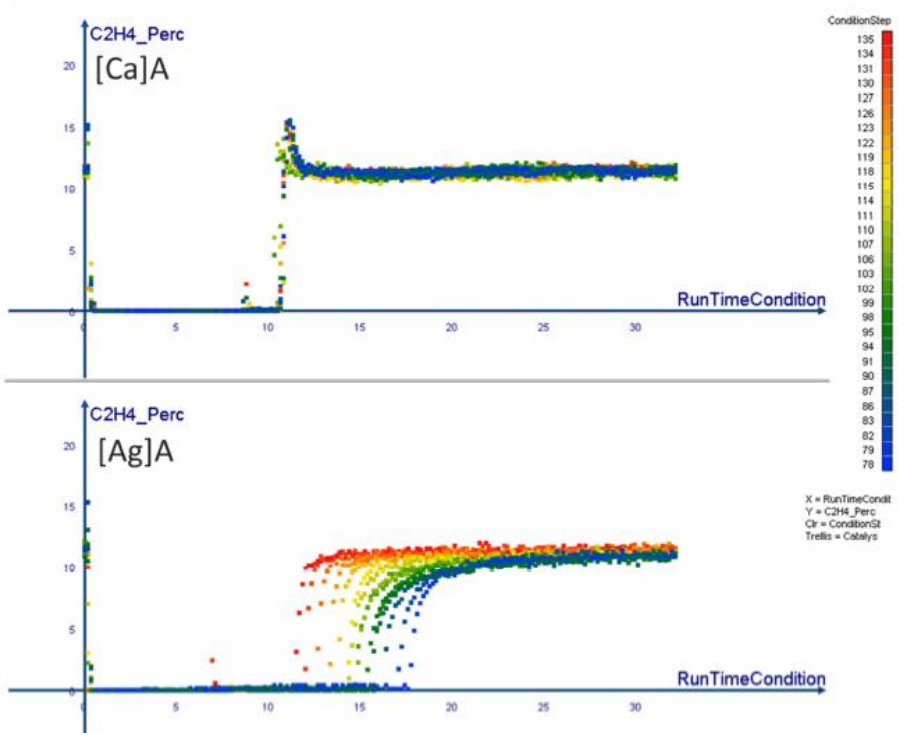


Figure 23 Long-term stability tests: breakthrough curve of ethylene of [Ca]A (top) and [Ag]A (bottom) over 15 adsorption/desorption cycles. Adsorption at 40°C, 5 bar. Feed: 3 mL/min (65% vol. N_2, 15% vol. C_2H_4, 5% vol. C_2H_6, 5% vol. CH_4, 5% vol. CO and 5% vol. Ar) + 0.5 mL/min CO_2 and 0.5 mL/min H_2. Desorption at 200°C at 5 bar with 3 mL/min N_2. Colors blue to red indicated subsequent cycles.

Both [Ca]A and [Ag]A materials were further tested at ECN under realistic gasification conditions for the study of the performance of the sorbents at larger scale.

6.3 Gasification tests for testing of ethylene removal

The 2 selected sorbents developed by partner Avantium, [Ca]A (molecular sieve 5A with calcium) and [Ag]A (molecular sieve 4A in which sodium was replaced by silver), were delivered to ECN for testing under realistic gasification conditions. Producer gas was generated in the MILENA gasifier operating with beech wood. A gas slipstream of approximately 1 Nm^3/h was fed to the system downstream. Tars were firstly removed in the OLGA system, then H_2S was removed in a ZnO bed, and afterwards, water was condensed out of the gas by cooling at 5°C. The clean gas was then fed to the BTX scrubber. After deep removal of water in a silica gel pot, the gas was compressed (between 3.6 bar in the test with Ca-zeolite and 5 bar in the experiment with Ag-zeolite) and fed to the sorbent bed. A detailed description of the results can be found in the note ECN-BEE-2015-222. In this section, the most relevant findings are summarized.

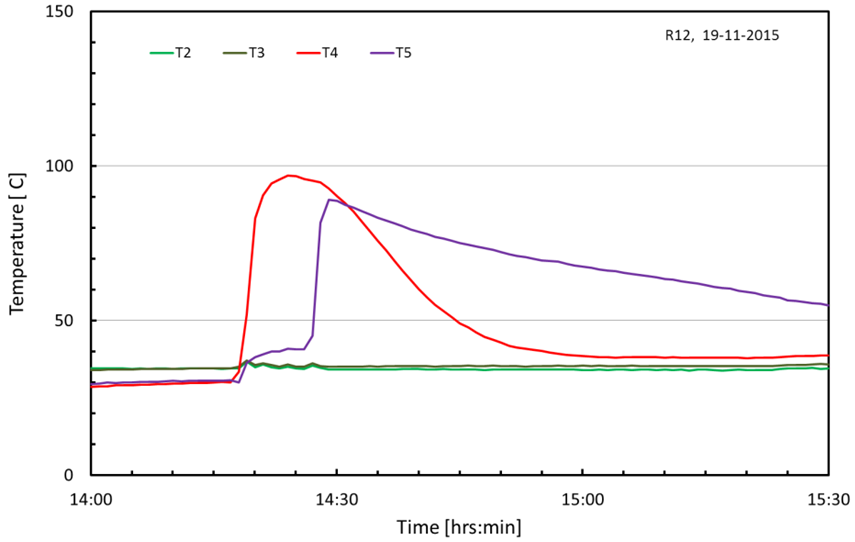


Figure 24 Inlet gas temperature (T2 and T3), and bed temperature (T4 and T5) during test with using [Ca]A zeolite as sorbent.

During the test with Ca-zeolite, the bed temperature increased from 30°C to 90°C (Figure 24), probably as a consequence of the exothermal heat of adsorption of CO_2. Also ethylene, ethane and acetylene were removed from the gas, as shown in Figure 25. After 10 minutes, the breakthrough of CO_2 took place, and soon after the breakthrough of the rest of hydrocarbons. Acetylene is the most strongly adsorbed compound. From the adsorption/desorption stages, it was estimated that the material adsorbed approximately 5 g acetylene, 15 g ethylene and 75 g CO_2 per kg material. During desorption, 70-90% of the adsorbed ethylene and CO_2 is released. This finding is consistent with the results from Avantium, where it was indicated that total desorption cannot be achieved within reasonable time, since desorption is slower than adsorption.

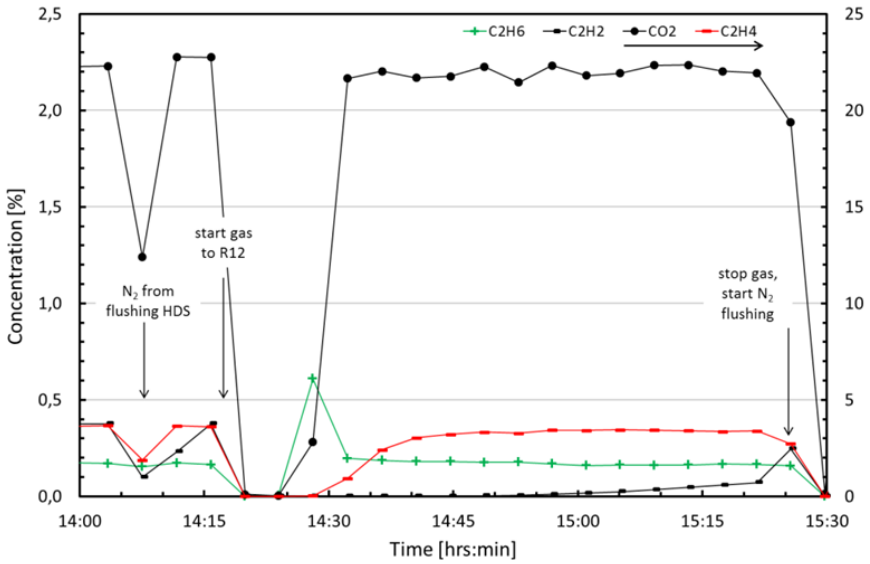


Figure 25 Gas composition after sorption reactor using [Ca]A zeolite as sorbent. Co-adsorption of CO_2, ethane, ethylene and acetylene can be observed.

On the other hand, the experiment with the Ag-zeolite showed that the material does not adsorb CO_2 or ethane, but the CO content is reduced, as detected by micro-GC analysis (Figure 27). The Ag-zeolite is able to capture ethylene and acetylene, but not ethane. There were signs of reduction of the silver oxide via reaction with H_2 and/or CO, in consistency with previous findings from Avantium during sorbent development. After some time, part of the adsorbed CO is released,

which reacts with oxygen from the silver oxide to form CO_2. This increased the bed temperature, as can be observed in Figure 26. Balances performed during the test point at the possible catalytic activity of the Ag-zeolite (either the metallic silver or the support material) towards exothermal reactions e.g. methanation, hydrogenation and possibly WGS and/or CO disproportionation, where ethane and methane are formed. The test was stopped when temperature increased to 500°C.

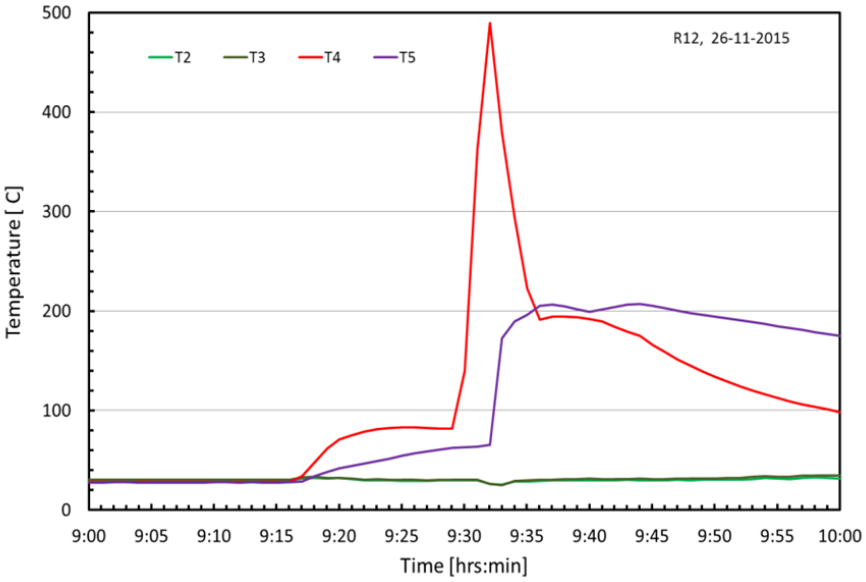


Figure 26 Inlet gas temperature (T2 and T3), and bed temperature (T4 and T5) during test with using [Ag]A zeolite as sorbent.

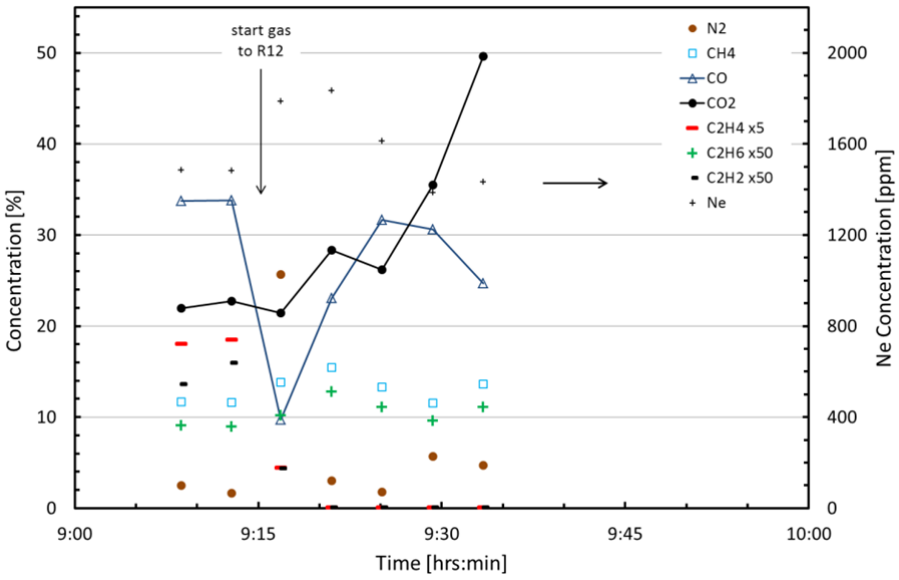


Figure 27 Gas composition measured by micro-GC after sorption reactor using [Ag]A zeolite as sorbent.

The experiments performed showed that further research is needed for the development of a sorbent for the separation of ethylene from producer gas. For this, it is important to pay attention to all the main components of producer gas. Acetylene is particularly interesting, since it is bound to the sorbent more strongly than ethylene. Even though acetylene concentration is 10 times lower than ethylene concentration, after several operating cycles, this would eventually reduce the capacity of the material towards ethylene adsorption. On the other hand, the test with Ag-zeolite showed that it is a risky option to load the zeolite with a metal that can react with the producer gas or that could even act as a catalyst.

7. Conclusions and outlook

The Green Birds project aims to increase the technical and economic feasibility of the co-production of energy/fuels and green chemicals from thermochemical conversion of biomass. This approach results in an increase of the overall efficiency of the conversion process as well as an improvement of the economic viability of bioenergy plants. In order to reach this goal, several strategies have been applied within the framework of the project. The final outcome of the project is a decision for the scale-up and demonstration of the processes and technologies developed within the project.

The first approach considered is the increase in the yield of benzene and toluene during gasification. For this, different experiments were carried out to determine whether there is a correlation between the lignin content of the gasification fuel and the yield of target compounds. A lignin-rich fuel (dried distilled biomass, DDB) was used in gasification tests in mixtures with wood. The experiments have shown that an increase in lignin content from ~20wt.% to 50 wt.% leads to a decrease in CO concentration, an increase of the benzene concentration, and a slight increase of ethylene content. However, when evaluating yields (which consider variations in both gas composition and carbon conversion), only CO and ethylene show a significant variation with the composition of the solid feedstock.

Green Birds has also studied the valorisation of humins (a carbonaceous, heterogeneous, syrup-like by-product of bio refinery process) via thermochemical conversion as a potential source for the production of green chemicals. This feedstock poses a big challenge, particularly its feeding and its behaviour during heating up. Although the feeding of humins to the gasifier was successful, problems arose within the reactor related to foaming, which in turn caused the blockage of the internal circulation of bed material. All in all, the gasification of humins at lab-scale proved challenging, but not unfeasible. Another approach explored within this project to overcome the feeding challenges of humins was based on the impregnation/mixing of humins on a porous carrier like wood and clay. The results of these experiments showed that mixing is a feasible alternative in order to properly feed humins into a gasifier or a combustor. However, further work would be required for the optimization of this strategy.

A BTX scrubbing system using a liquid absorption medium has been developed for the capture of BTX. An important milestone for bio-BTX recovery was reached in November 2014, where > 1 kg BTX was harvested for the first time from biomass gasification producer gas. The removal efficiency kept around 94%.The experimental results were used for the validation of the absorption/stripping model.

Adsorption has been considered for the removal of ethylene from producer gas. Among the functional zeolites screened and tested, the largest ethylene adsorption capacities were found for

zeolite [Ca]A and [Ag]A, with up to 7wt% ethylene adsorbed at 40 °C and 5 bar. First tests showed that the adsorption of [Ca]A is affected by the presence of water in the producer gas. Moreover, ethane and CO_2 were co-adsorbed by the material. In comparison, [Ag]A was able to selectively adsorb ethylene. However, high regeneration temperatures were needed to only partially recover the original ethylene adsorption capacity of [Ag]A. Moreover, a decrease in ethylene adsorption selectivity and capacity was observed over several adsorption-desorption cycles. The 2 selected sorbents developed by Avantium, [Ca]A and [Ag]A, were delivered to ECN for testing under realistic gasification conditions. The results obtained were in general consistent with the screening results obtained by Avantium. During the test with Ca-zeolite, ethylene, ethane, acetylene and CO_2 were co-adsorbed. The experiment with the Ag-zeolite showed that the material is able to capture ethylene and acetylene, but not ethane. [Ag]A does not adsorb CO_2 and ethane, but the CO content is reduced. There were signs of reduction of the silver oxide via reaction with H_2 and/or CO, as well as hints of catalytic activity of the Ag-zeolite towards exothermal reactions e.g. methanation, hydrogenation and possibly WGS and/or CO disproportionation, where ethane and methane are formed. All in all, the experiments showed that further research is needed in sorbent development.

Green Birds has also explored the route of reactive separation, which transforms benzene and ethylene into products that are easier to separate and add extra economic value. From a screening process, ethylbenzene production and aromatization of ethylene were identified as the most promising pathways based on criteria of added value, capital and operating costs, and process integration. These pathways were experimentally tested. The experiments indicated that high ethylene conversion > 90% is achievable, whereas ~40% ethylene was converted to aromatics. Based on the experimental results, several co-production schemes were modelled in ASPEN and evaluated with respect to the reference case of bioSNG production. The economic evaluation revealed that all the co-production schemes considered lead to a reduction in the production costs of bio-SNG in the range of 5-20%.

8. Dissemination activities

The results derived from Green Birds, summarized in the previous sections, have been released in form of publications, conference contributions and patents. In this section, a list is provided with the dissemination highlights of the project.

Scientific publications

I. van Zandvoort, G. van Klink, E. de Jong, J.C. van der Waal. Selectivity and stability of zeolites [Ag]A and [Ca]A during adsorption of ethylene from a complex gas mixture, Submitted to Micro and Mesoporous Materials.

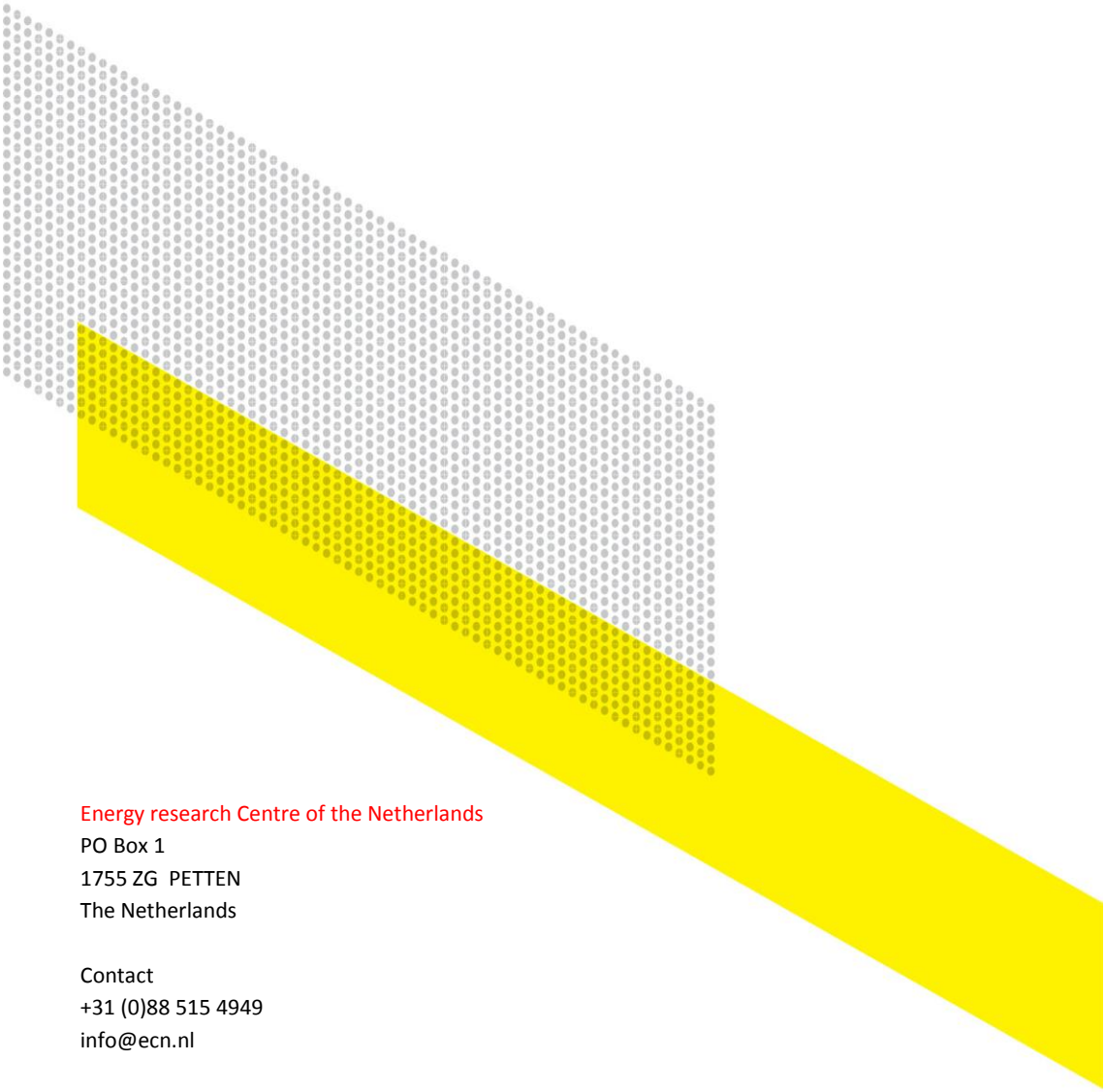
Conferences/workshops

A. van der Drift. Commercialisation of waste-to-energy through gasification technology developed by ECN. IEA Bioenergy Task 33 workshop. Ponferrada (Spain), 13 May 2015.

A. Bos, L.P.L.M. Rabou, B.J. Vreugdenhil, J.C. van der Waal, I. van Zandvoort. Recovery of valuable hydrocarbons from biomass/waste gasification producer gas. 24th European Biomass Conference & Exhibition (EUBCE 2016). Amsterdam, 6-9th June 2016 https://www.ecn.nl/publications/PdfFetch.aspx?nr=ECN-M--16-055

Patents

B.J. Vreugdenhil. *Removal of monocyclic aromatic compounds (BTX) from a gas*. P6053842NL (under review).



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